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APPLICATIONS OF PHOTOCURABLE
PRE-CERAMIC POLYMERS

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1 This application is a continuation-in-part of an
2 application filed June 3, 1999 under Serial No. 09/325,524
3 and is also a continuation-in-part of the application filed
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5 application filed June 3, 1999 under Serial No. 09/325,524.

6 BACKGROUND OF THE INVENTION

7 The field of the invention is specific applications of
8 photo curable pre-ceramic polymer chemistry to specific
9 applications and more particularly to specific applications
10 such as impregnation and/or coating of ceramic filters for
11 use in combustion engine exhaust systems.

12 U. S. Patent No. 6,174,565 teaches an abrasion
13 resistant ceramic material which includes a porous ceramic
14 material having a surface and a preceramic polymer which is
15 infiltrated into the surface. The preceramic polymer is

1 converted to a ceramic state.

2 U. S. Patent No. 6,165,240 teaches a filter apparatus
 3 which is for use in a forced air ventilation system. The
 4 filter apparatus has a first fan folded sheet of a washable
 5 first type of filter material, a second fan folded sheet of
 6 a second type of filter material, and fanfolds of the first
 7 and second fan folded sheets are substantially equally shaped
 8 and folded together such that the fanfolds of the first and
 9 second fan folded sheets are interdigitated to form a filter
 10 material assembly. The first type of filter material is
 11 preferably an electrostatically self-charging washable
 12 material such as woven polypropylene and the second type of
 13 filter material is preferably disposable and contains
 14 activated charcoal. The filter material assembly may be
 15 removably disposed in a rectangular filter frame for
 16 mounting the filter material assembly in the forced air
 17 system. The filter frame has at least one crank shaft
 18 rotatably disposed between two opposed side walls which are

1 shaped article and composite therefor which includes of a
2 shaped tool, such as a mold and providing a composite of a
3 quartz fabric disposed within a polysilazane which is
4 moldable at a temperature below the curing temperature of
5 the polysilazane and cured by catalyst. The polysilazane
6 can be optionally filled with particulate material. A
7 compaction pressure is applied to the composite to insure
8 contact of the composite and the tool and prevent loss of
9 less reactive polysilazane components. The composite is
10 then cured to hardness by increasing the temperature applied
11 to the composite at a rate of about 10°C/minute to a
12 temperature of about 150°C and holding that temperature of
13 about 150°C up to about 4 hours to provide a cured polymer.
14 The cured composite is removed from the tool. The polymer
15 can then be converted to a preceramic by heating the cured
16 polymer to a temperature sufficiently high in an inert
17 atmosphere or ammonia gas for a sufficient time. The
18 removal of carbon will occur when processed in ammonia. The

1 preceramic can then be reprocessed by repeating the above
2 procedure after cooling and reinfiltrating with uncured
3 resin.

4 U. S. Patent No. 4,806,612 teaches pre-ceramic
5 acetylenic polysilanes which contain $--(CH_2)_w C.tbd.CR'$
6 groups attached to silicon where w is an integer from 0 to 3
7 and where R' is hydrogen, an alkyl radical containing 1 to 6
8 carbon atoms, a phenyl radical, or an $--SiR''(3)$ radical
9 wherein R'' is an alkyl radical containing 1 to 4 carbon
10 atoms. The acetylenic polysilanes are prepared by reacting
11 chlorine-or bromine-containing polysilanes with either a
12 Grignard reagent of general formula $R'C.tbd.C(CH_2)_w MgX'$
13 where w is an integer from 0 to 3 and X' is chlorine,
14 bromine, or iodine or an organolithium compound of general
15 formula $R'C.tbd.C(CH_2)_w Li$ where w is an integer from 0
16 to 3. The acetylenic polysilanes can be converted to
17 ceramic materials by pyrolysis at elevated temperatures
18 under an inert atmosphere.

1 U. S. Patent No. 4,800,211 teaches 3-Hydroxybenzo[b]
2 thiophene-2-carboxamide derivatives which have been prepared
3 by: (1) treating a substituted 2-halobenzoate with a
4 thioacetamide; (2) treating a substituted thiosalicylate
5 with an appropriately substituted haloacetamide; and (3)
6 further synthetic modification of compounds prepared above.
7 These compounds have been found to be effective inhibitors
8 of both cyclooxygenase and lipoxygenase and thereby useful
9 in the treatment of pain, fever, inflammation, arthritic
10 conditions, asthma, allergic disorders, skin diseases,
11 cardiovascular disorders, psoriasis, inflammatory bowel
12 disease, glaucoma or other prostaglandins and/or leukotriene
13 mediated diseases.

14 U. S. Patent 4,588,832 teaches a novel and economical
15 route for the synthetic preparation of a 1-alkynyl
16 trihydrocarbyl silane compound. The method includes the
17 steps of reacting metallic sodium with a hydrocarbyl-
18 substituted acetylene or allene compound to form a

1 substituted sodium acetylide and reacting the acetylide with
2 a trihydrocarbyl monohalogenosilane in the reaction mixture
3 which is admixed with a polar organic solvent such as
4 dimethylformamide.

5 U. S. Patent No. 4,505,726 teaches an exhaust gas
6 cleaning device provided with a filter member which collects
7 carbon particulates in exhaust gases discharged from a
8 diesel engine and an electric heater for burning off the
9 particulates collected by the filter member. The filter
10 member is composed of a large number of intersecting porous
11 walls which define a large number of inlet gas passages and
12 outlet gas passages which are adjacent to each other. The
13 electric heater is composed of at least one film-shaped
14 heating resistor which is directly formed on the upstream
15 end surface of the filter member so as to be integral
16 therewith. When the amount of carbon particulates collected
17 by the filter member reaches a predetermined level, electric
18 current is supplied to the electric heater. The carbon

1 particulates adhered to the upstream end surface of the
2 filter member are ignited and burnt off. Then, the
3 combustion of carbon particulates spreads to the other
4 carbon particulates collected in the other portion of the
5 filter member.

6 U. S. Patent No. 5,843,304 teaches a materials
7 treatment system which includes filtration and treatment of
8 solid and liquid components of a material, such as a waste
9 material. A filter or substrate assembly is provided which
10 allows liquids to pass therethrough, while retaining solids.
11 The solids are then incinerated utilizing microwave energy,
12 and the liquids can be treated after passing through the
13 filter element, for example, utilizing a treatment liquid
14 such as an oxidant liquid. The filter assembly can also
15 include an exhaust filter assembly which removes solids or
16 particulate matter from exhaust gasses, with the retained
17 solids/particulates incinerated utilizing microwave energy.

18 U. S. Patent No. 5,074,112 teaches a filter assembly

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1 source is joined with a resonator mounted on an element of
2 the pipe for the exhaust gases which contains an insert,
3 characterized by the fact that the insert consists of a
4 filter whose upstream and downstream ends are offset toward
5 the inside of the cavity defined by the resonator and
6 delimit two chambers in which conductors of the electro-
7 magnetic field come out, respectively.

8 U. S. Patent No. 4,825,651 teaches a device and method
9 for separating soot or other impurities from the exhaust
10 gases of an internal-combustion engine, particularly a
11 diesel internal-combustion engine, comprises a microwave
12 source that is coupled to the intermediate section of the
13 exhaust pipe that is constructed for the development
14 of an electromagnetic field, an effective burning of the
15 soot with a low flow resistance, the intermediate section
16 being developed as a cavity resonator and at its exhaust gas
17 inlet and exhaust gas outlet, is equipped with a metal grid,
18 and an insert made of a dielectric material in the cavity

1 resonator concentrates the exhaust gas flow in the area of
2 high energy density of the electromagnetic field.

3 U. S. Patent No. 4,477,771 teaches conductive
4 particulates in the form of soot which are collected from
5 diesel engine exhaust gases on a porous wall monolithic
6 ceramic filter in such a way that the soot is somewhat
7 uniformly distributed throughout the filter. The filter is
8 housed in a chamber having a property of a microwave
9 resonant cavity and the cavity is excited with microwave
10 energy. As the particulates are collected the cavity appears
11 to the microwaves to have an increasing dielectric constant
12 even though the matter being accumulated is conductive
13 rather than dielectric so that as collected on the porous
14 filter it has the property of an artificial dielectric. The
15 response of the cavity to the microwave energy is monitored
16 to sense the effect of the dielectric constant of the
17 material within the cavity to provide a measure of the soot
18 content in the filter.

1 U. S. Patent No. 5,902,514 teaches a material for
2 microwave band devices which are used by the general people
3 and in industrial electronic apparatuses. Particularly, a
4 magnetic ceramic composition for use in microwave devices, a
5 magnetic ceramics for use in microwave devices and a
6 preparation method therefore are disclosed, in which the
7 saturation magnetization can be easily controlled, and a low
8 ferri-magnetic resonance half line width and an acceptable
9 curie temperature are ensured. The magnetic ceramic
10 composition for microwave devices includes yttrium oxide
11 (Y(2) O(3)), iron oxide (Fe(2) O(3)), tin oxide (SnO(2)),
12 aluminum oxide (Al(2) O(3)) and a calcium supply source.
13 The magnetic ceramics for the microwave devices are
14 manufactured by carrying out a forming and a sintering after
15 mixing: yttrium oxide, iron oxide, tin oxide, aluminum oxide
16 and calcium carbonate (or calcium oxide) based on a formula
17 shown below. It has a saturation magnetization of 100-1,800
18 G at the normal temperature, a temperature coefficient for

1 the saturation magnetization of 0.2%/° C, and a ferri-
2 magnetic resonance half line width of less than 60 Oe, $Y(3-x)Ca(x/2)Sn(x/2)Fe(5-y)Al(y)O(12)$ where $0.1 \leq x \leq 1$, and
3 $0.1 \leq y \leq 1.5$.

5 U. S. Patent No. 5,843,860 teaches a ceramic
6 composition for high-frequency dielectrics which includes
7 the main ingredients of $ZrO(2)$, $SnO(2)$ and $TiO(2)$ and a
8 subsidiary ingredient of $(Mn(NO(3))(2).4H(2)O)$. A
9 homogeneous ceramic composition can be prepared by a process
10 which comprises the steps of: adding $ZrO(2)$, $SnO(2)$ and
11 $TiO(2)$ by the molar ratio to satisfy $(ZrO(2))(1-x)$
12 $(SnO(2))(x)$ $(TiO(2))(1+y)$ (wherein, $0.1M^\circ C$ or above; and,
13 adding 1% or less of $Mn(NO(3))(2).4H(2)O$ by weight of
14 MnO to the mixture. The ceramic composition of the
15 invention has a high dielectric constant of 40 or more, a
16 quality factor of 7000 or more, and a temperature
17 coefficient of resonance frequency below 10. Accordingly,
18 it can be used for an integrated circuit at microwave as

1 well as at high frequency, or for dielectric resonators.

2 U. S. Patent No. 5,808,282 teaches a microwave
3 susceptor bed which is useful for sintering ceramics,
4 ceramic composites and metal powders. The microwave
5 susceptor bed contains granules of a major amount of a
6 microwave susceptor material, and a minor amount of a
7 refractory parting agent, either dispersed in the susceptor
8 material, or as a coating on the susceptor material.
9 Alumina is the preferred susceptor material. Carbon is the
10 most preferred parting agent. A sintering process uses the
11 bed to produce novel silicon nitride products.

12 U. S. Patent No. 5,446,270 teaches a composition which
13 includes susceptors having the capability of absorbing
14 microwave energy and a matrix. The susceptors includes a
15 particulate substrate substantially non-reflective of
16 microwave energy and a coating capable of absorbing
17 microwave energy. The matrix is substantially non-
18 reflective of microwave energy. Susceptors are typically

1 particles having a thin-film coating thereon. The matrix
 2 typically includes polymeric or ceramic materials that are
 3 stable at temperatures conventionally used in microwave
 4 cooking. The composition allows reuse of the susceptors,
 5 eliminates decline in heating rate, eliminates arcing,
 6 allows the heating rate to be controlled, allows overheating
 7 to be controlled, and allows formation of microwave heatable
 8 composite materials having very low metal content.

9 U. S. Patent No. 5,365,042 teaches a heat treatment
 10 installation for parts made of a composite material which
 11 has a ceramic matrix and which includes a treatment
 12 enclosure. The treatment enclosure is connected to a
 13 microwave generator by a wave-guide and which includes a
 14 press for hot pressing a part to be treated in the enclosure
 15 and a gas source for introducing a protective gas into the
 16 enclosure.

17 U. S. Patent No. 5,126,529 teaches a method for forming
 18 a three-dimensional object by thermal spraying which

1 utilizes a plurality of masks positioned and removed over a
 2 work surface in accordance with a predetermined sequence.
 3 The masks correspond to cross sections normal to a
 4 centerline through the work-piece. One set of masks defines
 5 all cross sections through the work-piece. A second set of
 6 masks contains at least one mask. The mask corresponds to
 7 each mask of the first set. Masks from each set are
 8 alternatively placed above a work surface and sprayed with
 9 either a deposition material from which the work-piece will
 10 be made or a complementary material. In this manner, layers
 11 of material form a block of deposition material and
 12 complementary material. The complementary material serves
 13 as a support structure during forming and is removed.
 14 Preferably, the complementary material has a lower melting
 15 temperature than the deposition material and is removed by
 16 heating the block. Alternatively, one could mask only for
 17 the deposition material and remove complementary material
 18 overlying the deposition material after each spraying of

1 complementary material.

2 U. S. Patent No. 4,199,387 teaches an air filter unit
3 of the pleated media, high efficiency type. The media pleat
4 edges are sealed to the supporting frame to prevent bypass
5 of air with a ceramic adhesive and fibrous ceramic mat which
6 allows the unit to be exposed to high temperatures (e.g., up
7 to 2000° F.) without danger of seal breakdown. While in the
8 form of a slurry the adhesive is applied, for example, with
9 a trowel to the zig-zag pleated edges of the media which,
10 together with corrugated spacers, forms the filter core.
11 The latter is then surrounded on four sides by the
12 compressible mat of fibrous ceramic material and inserted in
13 a box-like support frame with the slurry filling the space
14 between the pleated edges of the media and the fibrous mat.
15 The filter core and the surrounding mat are assembled with
16 the support frame while the slurry is still wet whereby,
17 upon hardening, the resulting layers of ceramic cement
18 provide a complete, heat-resistant seal while avoiding

1 cracking in normal handling due to the resilience of the
2 compressed fibrous mat which maintains an airtight seal
3 between hardened ceramic and support frame.

4 U. S. Patent No. 6,063,150 teaches a self-cleaning
5 particle filter for Diesel engines which includes a filter
6 housing, control circuitry, a removable filter sandwich and
7 independent power source. The removable filter sandwich
8 includes a number of sintered metal strips sewn and
9 positioned between two sheets of inorganic material to
10 provide a filter sandwich. Current is delivered to the
11 metal filter strips to efficiently burn off carbon, lube oil
12 and unburned fuel particulates which have been filtered from
13 exhaust gas. The filter sandwich is formed into a
14 cylindrical configuration and mounted onto a perforated
15 metal carrier tube for receiving and filtering exhaust gas.

16 U. S. Patent No. 6,101,793 teaches an exhaust gas
17 filter having a ceramic filter body is configured such that
18 a specific heat h (cal/g °C) of ceramic powder constituting

1 the body, an a bulk specific gravity d (g/cm^3) of the
 2 filter, satisfy the relation $0.12 \text{ (cal}/\text{cm}^3 \text{ } ^\circ\text{C)}$
 3 $\leq h \cdot d \leq 0.19 \text{ (cal}/\text{cm}^3 \text{ } ^\circ\text{C)}$. The ceramic filter body
 4 includes a plurality of cells which extend axially to open
 5 at opposite ends of the body. One of the opposite axial
 6 ends of each of the cells is closed by a filler in such a
 7 manner that the closed ends of the cells and the open ends
 8 of the cells are arranged in an alternating configuration.
 9 The filter traps particulates in the exhaust gas, and the
 10 trapped particulates are removed by regeneration combustion
 11 of the filter. The filter exhibits excellent durability,
 12 thus preventing the formation of cracks in the surface and
 13 interior of the filter. When the filter is mounted on a
 14 diesel engine, the diesel engine advantageously does not
 15 discharge black smoke.

16 U. S. Patent No. 5,756,412 teaches a dielectric ceramic
 17 composition for microwave applications which consists
 18 essentially of the compound having a formula $B'B(2) O(6)$,

1 wherein B' is at least one metal selected from the group of
 2 Mg, Ca, Co, Mn, Ni and Zn, and wherein B'' is one of Nb or Ta,
 3 and additionally includes at least one compound selected
 4 from the group of CuO, V(2) O(5), La(2) O(3), Sb(2) O(5),
 5 WO(3), MnCO(3), MgO, SrCO(3), ZNO, and Bi(2) O(3) as an
 6 additive, wherein the amount of the additive is 0.05% to
 7 2.0% by weight of the total weight of the composition.

8 The synthesis of polycarbosilane from the pyrolytic
 9 condensation reaction of polydimethylsilane obtained from
 10 the reaction of dichlorodimethylsilane with an alkali metal,
 11 such as sodium. In the latter approach, polydimethylsilane
 12 can be prepared by Würtz type coupling of dichlorodimethyl-
 13 silane with sodium in toluene. The direct pyrolysis of
 14 polydimethylsilane, a viscous thermoplastic resin, at high
 15 temperature gives SiC in a ceramic yield of about 30%-40%.
 16 By thermally cross-linking the polydimethylsilane into an
 17 infusible rigid thermoset polymer, which is insoluble in any
 18 common solvents, the subsequent pyrolysis yield is on the

1 order of 88%-93%. This thermolysis was accomplished by
2 refluxing the polydimethyl-silane to in excess of 350°C.

3 Numerous pre-ceramic polymers with improved yields of
4 the ceramic have been described in U. S. Patent No.
5 5,138,080, U. S. Patent No. 5,091,271, U. S. Patent No.
6 5,051,215 and U. S. Patent No. 5,707,471. The fundamental
7 chemistry contained in these embodiments is specific to the
8 process employed and mainly leaves the pre-ceramic polymer
9 in a thermoplastic state. These pre-ceramic polymers which
10 catalytic or photo-induced cross-linking do not satisfy the
11 high ceramic yield, purity and fluidity in combination with
12 low temperature crosslinking ability necessary for producing
13 large densified ceramic structures in a single step
14 continuous process.

15 U. S. Patent No. 5,138,080 teaches a novel polysila-
16 methylenosilane polymers which has polysilane-poly-
17 carbosilane skeleton which can be prepared in one-step
18 reaction from mixtures of chlorosilaalkanes and organochloro

1 silanes with alkali metals in one of appropriate solvents or
2 in combination of solvents thereof. Such polysilamethyleno
3 silane polymers are soluble and thermoplastic and can be
4 pyrolyzed to obtain improved yields of silicon carbide at
5 atmospheric pressure.

6 U. S. Patent No. 5,091,271 teaches a shaped silicon
7 carbide-based ceramic article which has a mechanical
8 strength which is produced at a high efficiency by a process
9 including the step of forming an organic silicone polymer,
10 for example, polycarbosilastylene copolymer, into a
11 predetermined shape, for example, a filament or film; doping
12 the shaped polymer with a doping material consisting of at
13 least one type of halogen, for example, bromine or iodine,
14 in an amount of 0.01% to 150% based on the weight of the
15 shaped polymer, to render the shaped polymer infusible; and
16 pyrolyzing the infusible shaped polymer into a shaped SiC-
17 based ceramic article at a temperature of 800° C to 1400° C
18 in an inert gas atmosphere, optionally the halogen-doped

1 shaped polymer being treated with a basic material, for
 2 example, ammonia, before the pyrolyzing step, to make the
 3 filament uniformly infusible.

4 U. S. Patent No. 5,300,605 teaches poly(I-hydro-1-R-1-
 5 silapent-3-ene) homopolymers and copolymers which contain
 6 silane segments with reactive silicon-hydride bonds and
 7 contain hydrocarbon segments with cis and trans carbon-
 8 carbon double bonds.

9 U. S. Patent No. 5,171,810 teaches random or block
 10 copolymers with (I-hydro-I-R-I-sila-cis-pent-3-ene), poly(I-
 11 hydro-1-R-3,4 benzo-1-sila pent-3-ene) and disubstituted I-
 12 silapent-3-ene repeating units of the general formula ##STRI##
 13 where R is hydrogen, an alkyl radical containing from one to
 14 four carbon atoms or phenyl, R. sup. 1 is hydrogen, an alkyl
 15 radical containing from one to four carbon atoms, phenyl or a
 16 halogen and R.sup.2 is hydrogen, or R. sup.1 and R. sup. 2 are
 17 combined to form a phenyl ring, are prepared by the anionic
 18 ring opening polymerization of silacyclopent-3-enes or 2-

1 silaindans with an organometallic base and cation coordinating
2 ligand catalyst system or a metathesis ring opening catalyst
3 system.

4 U. S. Patent No. 5,169,916 Poly(I -hydro- I -R- I -
5 sila-cis-pent-3-ene) and poly(I -hydro- I -R-3,4 benzo-1-
6 sila pent-3-ene) polymers which has repeating units of the
7 general formula polycarbosilane containing at least two
8 tbd.SiH groups per molecule via intimately contacting such
9 fusible polycarbosilane with an effective hardening amount
10 of the vapors of sulfur.

11 U. S. Patent No. 5,064,915 teaches insoluble poly-
12 carbosilanes, readily pyrolyzed into silicon carbide ceramic
13 materials such as SiC fibers, are produced by hardening a
14 fusible polycarbosilane containing at least two tbd. SiH
15 groups per molecule via intimately contacting such fusible
16 polycarbosilane with an effective hardening amount of the
17 vapors of sulfur.

1 U. S. Patent No. 5,049,529 teaches carbon nitride ceramic
2 materials which are produced by hardening a fusible
3 polycarbosilane containing at least two tbd.SiH groups per
4 molecule by intimately contacting such fusible polycarbosilane
5 with an effective hardening amount of the vapors of sulfur,
6 next, heat treating the infusible polycarbosilane which
7 results under an ammonia atmosphere to such extent as to
8 introduce nitrogen into the infusible polycarbosilane without
9 completely removing the carbon therefrom and then heat
10 treating the nitrogenated polycarbosilane in a vacuum or in an
11 inert atmosphere to such extent as to essentially completely
12 convert it into a ceramic silicon carbon nitride.

13 U. S. Patent No. 5,051,215 teaches a rapid method of
14 infusibilizing pre-ceramic polymers which includes treatment
15 of the polymers with gaseous nitrogen dioxide. The
16 infusibilized polymers may be pyrolyzed to temperatures in
17 excess of about 800°C to yield ceramic materials with low
18 oxygen content and, thus, good thermal stability. The methods

1 are especially useful for the production of ceramic fibers
 2 and, more specifically, to the on-line production of ceramic
 3 fibers.

4 U. S. Patent No. 5,028,571 teaches silicon nitride
 5 ceramic materials which are produced by hardening a fusible
 6 polycarbosilane containing at least two dbd.SiH groups per
 7 molecule by intimately contacting such fusible polycarbo-
 8 silane with an effective hardening amount of the vapors of
 9 sulfur and then pyrolyzing the infusible polycarbosilane
 10 which results under an ammonia atmosphere.

11 U. S. Patent No. 4,847,027 teaches a method for the
 12 preparation of ceramic materials or articles by the pyrolysis
 13 of pre-ceramic polymers wherein the pre-ceramic polymers are
 14 rendered infusible prior to pyrolysis by exposure to gaseous
 15 nitric oxide. Ceramic materials with low oxygen content,
 16 excellent physical properties, and good thermal stability can
 17 be obtained by the practice of this process. This method is
 18 especially suited for the preparation of ceramic fibers.

1 U.S. Patent No. 5,714,025 teaches a method for preparing
2 a ceramic-forming pre-preg tape which includes the steps of
3 dispersing in water a ceramic-forming powder and a fiber,
4 flocculating the dispersion by adding a cationic wet strength
5 resin and an anionic polymer, dewatering the flocculated
6 dispersion to form a sheet, wet pressing and drying the sheet,
7 and coating or impregnating the sheet with an adhesive
8 selected from the group consisting of a polymeric ceramic
9 precursor, and a dispersion of an organic binder and the
10 materials used to form the sheet. The tape can be used to
11 form laminates, which are fired to consolidate the tapes to a
12 ceramic.

13 U. S. Patent No.5,707,471 teaches a method for preparing
14 fiber reinforced ceramic matrix composites which includes the
15 steps of coating refractory fibers, forming the coated fibers
16 into the desired curing the coated fibers to form a pre-preg,
17 heating the pre-preg to form a composite and heating the
18 composite in an oxidizing shape, environment to form an in

1 situ sealant oxide coating on the composite. The refractory
2 fibers have a interfacial coating thereon with a curable pre-
3 ceramic polymer which has a char containing greater than about
4 50% sealant oxide atoms. The resultant composites have good
5 oxidation resistance at high temperature as well as good
6 strength and toughness.

7 U. S. Patent No. 5,512,351 teaches a new pre-preg
8 material which has good tack drape properties and feasible
9 out-time. The pre-preg material is prepared by impregnating
10 inorganic fibers with a composition which includes a fine
11 powder of a metal oxide or oxides having an average particle
12 diameter of not larger than one micrometer, a soluble
13 siloxane polymer having double chain structure, a
14 trifunctional silane compound having at least one
15 ethylenically unsaturated double bond in the molecule
16 thereof, a organic peroxide and a radically polymerizable
17 monomer having at least two ethylenically unsaturated double
18 bonds and heating the impregnated fibers.

1 U. S. Patent No. 4,835,238 teaches a reaction of 1,1-
2 dichloro-silacyclobutanes with nitrogen-containing
3 difunctional nucleophiles which gives polysilacyclobuta-
4 silazanes which can be crosslinked and also converted to
5 ceramic materials.

6 Numerous processing mechanics with various direct
7 applications have been described, for example, in the U. S.
8 Patent No. 5,820,483, U. S. Patent No. 5,626,707, U. S.
9 Patent No. 5,732,743 and U. S. Patent No. 5,698,055. The
10 process mechanics are for a single product process and do
11 not permit continuous curing and pyrolysis in a single step
12 to produce highly dense thick ceramic components.

13 U. S. Patent No. 5,820,483 teaches methods for
14 manufacturing a shaft for a golf club. A plug is detachably
15 affixed to a distal end of a mandrel. A plurality of plies
16 of pre-preg composite sheet are wrapped around the mandrel
17 and plug and, thereafter, heated causing the resin
18 comprising the various plies to be cured. The mandrel is

1 then removed from the formed shaft, leaving the plug as an
2 integral part of the distal tip of the shaft.

3 U. S. Patent No. 5,626,707 teaches an apparatus which
4 produces a composite tubular article. The apparatus includes
5 a frame, a drive mechanism for rotating a mandrel, at least
6 two spindles mounted to the frame, a tensioner and a belt
7 extending between the first and second spindles. The
8 apparatus may be used to roll pre-preg strips or similar
9 sheets of composite materials around the mandrel. The belt
10 travels over the spindles, and the spindles guide the belt
11 through changes in its direction of travel. The mandrel is
12 mounted in the drive mechanism in contact with the belt, which
13 changes its direction of travel around the mandrel. The lower
14 surface of the belt bears against upper portions of the
15 spindles, and the mandrel contacts the upper surface of the
16 belt. As the drive mechanism rotates the mandrel, pre-preg
17 sheets are fed between the mandrel and the belt and are
18 thereby wrapped around the mandrel. The belt presses the pre-

1 preg sheets against the mandrel. The wrapped mandrel may then
 2 be removed from the apparatus and cured in any suitable manner
 3 known in the art to produce the a composite tubular article.

4 U. S. Patent No. 5,732,743 teaches a method for joining
 5 and repairing pipes includes the step of utilizing photo-
 6 curable resins in the form of a fabric patch to for quickly
 7 repairing or sealing pipes. A photo-curable flexible pre-preg
 8 fabric is wrapped over the entire area of the pipe to be
 9 joined or repaired. The pre-preg fabric contains multiple
 10 layers of varying widths and lengths. The pre-preg fabric is
 11 then exposed to photo-radiation which cures and seals the
 12 pipe.

13 U. S. Patent No. 5,698,055 teaches a method for making a
 14 reinforced tubular laminate. A dry braided fiber sleeve is
 15 placed between a mandrel and spiral tape wrap either over,
 16 under, or layered with a pre-preg material. During the
 17 initial stages of the curing process, while the temperature is
 18 rising, the resin in the pre-preg material flows and wets out

1 the dry braid. When the final cure takes place, the braid
2 becomes an integral part of the finished laminate. The choice
3 of fiber materials and braid angle permits various tubular
4 laminate strengths. The selection of fiber colors and
5 patterns permit a wide variety of tubular laminate aesthetic
6 characteristics.

7 U. S. Patent No. 5,632,834 teaches sandwich structures
8 which are made of fiber-reinforced ceramics. The base
9 substance of the ceramic matrix consists of a Si-organic
10 polymer and a ceramic or metallic powder. A cross-linking of
11 the Si-organic polymer takes place under increased pressure
12 and at an increased temperature. After the joining of the
13 facings and the honeycomb core, the sandwich structure is
14 pyrolysed to form a ceramic material

15 U. S. Patent No. 5,641,817 teaches organometallic ceramic
16 precursor binders which are used to fabricate shaped bodies by
17 different techniques. Exemplary shape making techniques which
18 utilize hardenable, liquid, organometallic, ceramic precursor

1 binders include the fabrication of negatives of parts to be
 2 made (e.g., sand molds and sand cores for metalcasting, etc.),
 3 as well as utilizing ceramic precursor binders to make shapes
 4 directly (e.g., brake shoes, brake pads, clutch parts,
 5 grinding wheels, polymer concrete, refractory patches and
 6 liners, etc.). A thermosettable, liquid ceramic precursors
 7 provides suitable-strength sand molds and sand cores at very
 8 low binder levels and, upon exposure to molten metal casting
 9 exhibit low emissions toxicity as a result of their high char
 10 yields of ceramic upon exposure to heat. The process involves
 11 the fabrication of preforms used in the formation of composite
 12 articles. Production costs, and relatively poor physical
 13 properties prohibits their inherently large cost of
 14 capitalization, high wide use.

15 U. S. Patent No. 4,631,179 teaches this ring-opening-
 16 polymerization reactions method to obtain a linear polymer
 17 of the formula $[\text{SiH}_{.2} \text{CH}_{.2}]_{.n}$. This polymer
 18 exhibit ceramics yields up to 85% on pyrolysis. The

1 starting material for the ring-opening-polymerization
2 reaction was the cyclic compound $[\text{SiH}_2\text{CH}_2]_n$, which is difficult and costly to obtain in pure
3 form by either of the procedures that have been reported.

4
5 U. S. Patent No. 5,888,641 teaches an exhaust manifold
6 for an engine which are made of all fiber reinforced ceramic
7 matrix composite material so as to be light weight and high
8 temperature resistant. A method of making the exhaust
9 manifold includes the steps of forming a liner of a cast
10 monolithic ceramic material containing pores, filling the
11 pores of the cast monolithic ceramic material with a pre-
12 ceramic polymer resin, coating reinforcing fibers with an
13 interface material to prevent a pre-ceramic polymer resin
14 from adhering strongly to the reinforcing fibers, forming a
15 mixture of a pre-ceramic polymer resin and reinforcing
16 fibers coated with the interface material, forming an
17 exhaust manifold shaped structure from the mixture of the
18 pre-ceramic polymer resin and the reinforcing fibers coated

1 with the interface material by placing the mixture on at
 2 least a portion of the cast monolithic ceramic material,
 3 and firing the exhaust component shaped structure at a
 4 temperature and a time sufficient to convert the pre-ceramic
 5 polymer resin to a ceramic thereby forming a reinforced
 6 ceramic composite.

7 U. S. Patent No. 5,153,295 teaches compositions of
 8 matter which have potential utility as precursors to silicon
 9 carbide. These compositions are obtained by a Grignard
 10 coupling process starting from chlorocarbosilanes, a readily
 11 available class of compounds. The new precursors
 12 constitute a fundamentally new type of polycarbosilane that
 13 is characterized by a branched, $[\text{Si}-\text{C}]_{\text{sub.n}}$ "backbone"
 14 which consists of $\text{SiR}_{\text{sub.3}}\text{CH}_{\text{sub.2}}--$, $--\text{SiR}_{\text{sub.2}}$
 15 $\text{CH}_{\text{sub.2}}--$, $\text{.dbd.SiRCH}_{\text{sub.2}}--$, and $\text{.tbd.SiCH}_{\text{sub.2}}--$
 16 units (where R is usually H but can also be other organic
 17 or inorganic groups, e.g., lower alkyl or alkenyl, as may be
 18 needed to promote crosslinking or to modify the physical

1 properties of the polymer or the composition of the final
 2 ceramic product). A key feature of these polymers is that
 3 substantially all of the linkages between the Si--C units
 4 are "head-to-tail", i.e., they are Si to C. The
 5 polycarbosilane "SiH.sub.2 CH.sub.2 " has a carbon to
 6 silicon ratio of 1 to 1 and where substantially all of the
 7 substituents on the polymer backbone are hydrogen. This
 8 polymer consists largely of a combination of the four
 9 polymer "units": SiH.sub.3 CH.sub.2 --, --SiH.sub.2 CH.sub.2
 10 --, .dbd.SiHCH.sub.2 --, and .tbd.SiCH.sub.2 -- which are
 11 connected "head-to-tail" in such a manner that a complex,
 12 branched structure results. The branched sites introduced
 13 by the last two "units" are offset by a corresponding number
 14 of SiH.sub.3 CH.sub.2 -- "end groups" while maintaining the
 15 alternating Si--C "backbone". The relative numbers of the
 16 polymer "units" are such that the "average" formula is
 17 SiH.sub.2 CH.sub.2. These polymers have the advantage that
 18 it is only necessary to lose hydrogen during pyrolysis, thus

1 ceramic yields of over 90% are possible, in principle. The
 2 extensive Si--H functionality allows facile crosslinking and
 3 the 1 to 1 carbon to silicon ratio and avoids the
 4 incorporation of excess carbon in the SiC products that are
 5 ultimately formed. The synthetic procedure employed to make
 6 them allows facile modification of the polymer, such as by
 7 introduction of small amounts of pendant vinyl groups, prior
 8 to reduction. The resulting vinyl-substituted "SiH.sub.2
 9 CH.sub.2 " polymer has been found to have improved
 10 crosslinking properties and higher ceramic yield.

11 A pre-ceramic polymer is prepared by a thermally
 12 induced methylene insertion reaction of polydimethylsilane.
 13 The resulting polymer is only approximately represented by
 14 the formula [SiHMeCH.sub.2].sub.n, as significant amounts
 15 of unreacted (SiMe.sub.2).sub.n units, complex rearrange-
 16 ments, and branching are observed. Neither the preparation
 17 nor the resulting structure of this precursor are therefore
 18 similar to the instant process. In addition to the

1 carbosilane "units", large amounts of Si--Si bonding remains
 2 in the "backbone" of the polymer. This polymer, in contrast
 3 to the instant process, contains twice the stoichiometric
 4 amount of carbon for SiC formation. The excess carbon must
 5 be eliminated through pyrolytic processes that are by no
 6 means quantitative. Despite the shortcomings, this polymer
 7 has been employed to prepare "SiC" fiber. However, it must
 8 be treated with various crosslinking agents prior to
 9 pyrolysis which introduce contaminants. This results in a
 10 final ceramic product that contains significant amounts of
 11 excess carbon and silica which greatly degrade the high
 12 temperature performance of the fiber.

13 SiC precursors predominately linear polycarbo-silanes
 14 have been prepared via potassium dechlorination of chloro-
 15 chloromethyl-dimethylsilane. The resulting polymers have
 16 not been fully characterized, but probably contain
 17 significant numbers of Si--Si and CH₂--CH₂ groups
 18 in the polymer backbone. The alkali metal dechlorination

1 process used in the synthesis of such materials does not
 2 exhibit the selective head-tail coupling found with Grignard
 3 coupling. The pendant methyl groups in such materials also
 4 lead to the incorporation of excess carbon into the system.
 5 In several polymer systems mixtures containing vinylchloro-
 6 silanes (such as $\text{CH}_2\text{--CH--Si}(\text{Me})\text{Cl}_2$) and
 7 Me_2SiCl_2 are coupled by dechlorination with
 8 potassium in tetrahydro-furan. U. S. Patent No. 4,414,403
 9 and U. S. Patent No. 4,472,591 both teach this method. The
 10 "backbone" of the resulting polymers consists of a
 11 combination of Si--Si and $\text{Si--CH}_2\text{CH}(\text{--Si})_2$ units.
 12 Later versions of this polymer $\text{Me}(\text{H})\text{SiCl}_2$ in addition
 13 to the Me_2SiCl_2 and are subjected to a sodium-
 14 hydrocarbon dechlorination process which does not attack
 15 vinyl groups. The resulting polymer consists of a
 16 predominately linear, Si--Si "backbone" bearing pendant
 17 methyl groups, with some Si--H and $\text{Si--CH}_2\text{CH}_2$
 18 functionality to allow crosslinking on pyrolysis.

1 None of these precursors derived using vinylchloro-
2 silanes are similar to those of the process in that having
3 predominantly Si--Si bonded "backbones", they are
4 essentially polysilanes, not polycarbosilanes. In addition,
5 the carbon in these polymers is primarily in the form of
6 pendant methyl functionality and is present in considerable
7 excess of the desirable 1 to 1 ratio with silicon. The
8 ceramic products obtained from these polymers are known to
9 contain considerable amounts of excess carbon.

10 Polymeric precursors to SiC have been obtained by
11 redistribution reactions of methyl-chloro-disilane
12 (Me.sub.6-x Cl.sub.x Si.sub.2, x=2-4) mixtures, catalyzed by
13 tetraalkyl-phosphonium halides which U. S. Patent No.
14 4,310,481, U. S. Patent No. 4,310,482 and U. S. Patent No.
15 4,472,591 teach. In a typical preparation, elemental
16 analysis of the polymer was employed to suggest the
17 approximate formula [Si(Me).sub.1.15 (H).sub.0.25].sub.n,
18 with n averaging about 20. The reaction is fundamentally

1 different than that involved in the process and the
2 structures of the polymers are also entirely different,
3 involving what is reported to be a complex arrangement of
4 fused polysilane rings with methyl substitution and a
5 polysilane backbone.

6 The formation of carbosilane polymers with pendent
7 methyl groups as by-products of the "reverse-Grignard"
8 reaction of chloromethyl-dichloro-methylsilane. The chief
9 purpose of this work was the preparation of carbosilane
10 rings and the polymeric byproduct was not characterized in
11 detail nor was its use as a SiC precursor suggested.
12 Studies of this material indicate that it has an
13 unacceptably low ceramic yield on pyrolysis. These polymers
14 are related to those described in the instant process and
15 are obtained by a similar procedure, however, they contain
16 twice the required amount carbon necessary for
17 stoichiometric silicon carbide and their use as SiC
18 precursors was not suggested. Moreover, the starting

1 material, chloromethyl-dichloro-methylsilane, contains only
 2 two sites on the Si atom for chain growth and therefore
 3 cannot yield a structure which contains .tbd.SiCH.sub.2 --
 4 chain units. On this basis, the structure of the polymer
 5 obtained, as well as its physical properties and pyrolysis
 6 characteristics, must be significantly different from that
 7 of the subject process.

8 U. S. Patent No. 4,631,179 teaches a polymer which is
 9 a product of the ring-opening polymerization of (SiH.sub.2
 10 CH.sub.2).sub.2 also has the nominal composition "SiH.sub.2
 11 CH.sub.2 ". However, the actual structure of this polymer
 12 is fundamentally and functionally different from that of the
 13 instant process. Instead of a highly branched structure
 14 comprised of SiR.sub.3 CH.sub.2 --, --SiR.sub.2 CH.sub.2 --,
 15 .dbd.SiRCH.sub.2 --, and .tbd.SiCH.sub.2 -- units, the Smith
 16 polymer is reported to be a linear polycarbosilane which
 17 presumably has only [SiH.sub.2 CH.sub.2] as the internal
 18 chain segments. Such a fundamental structural difference

1 would be expected to lead to quite different physical and
2 chemical properties. The fundamental difference in these
3 two structures has been verified by the preparation of a
4 linear polymer analogous to polymer and the comparison of
5 its infrared and H-NMR spectra.

6 Another important difference between the process of
7 Smith and the instant process is the method used to obtain
8 the product polymer and the nature of the starting
9 materials. The $[\text{SiH}_2\text{CH}_2]_n$ monomer used by
10 Smith is difficult and expensive to prepare and not
11 generally available, whereas the chlorocarbosilanes used in
12 the instant process are readily available through commercial
13 sources.

14 U. S. Patent No. 4,923,716 teaches chemical vapor
15 deposition of silicon carbide which uses a "single
16 molecular species" and which provides reactive fragments
17 containing both silicon and carbon atoms in equal number
18 this process. Linear and cyclic structures of up to six

1 units are mentioned. These compounds, which include both
 2 silanes and carbosilanes, are specifically chosen to be
 3 volatile for chemical vapor deposition use, and are
 4 distinctly different from the instant process, where the
 5 products are polymers of sufficiently high molecular weight
 6 that they cross-link before significant volatilization
 7 occurs. Such volatility would be highly undesirable for the
 8 applications under consideration for the polymers of the
 9 instant process, where excessive loss of the silicon-
 10 containing compound by vaporization on heating would be
 11 unacceptable.

12 The inventors hereby incorporate the above-referenced
 13 patents and articles into this application.

14 SUMMARY OF THE INVENTION

15 The present invention is generally directed to a
 16 process of forming a photo-curable pre-ceramic polymer for
 17 use in for fabricating ceramic matrix composites.

18 In a first separate aspect of the invention the process

1 includes the steps to silicon carbide ceramic.

2 In a second separate aspect of the invention the
3 process includes the steps of reacting sodium acetylide with
4 organo-chlorosilanes and condensing (polymerizing) the
5 resultant organo-(ethynyl)-chloro silane product of step a
6 with an excess of an alkali metal. The process includes
7 the steps preparing a solution of thermoplastic photo-
8 curable pre-ceramic polymer, passing a fiber, tape or fabric
9 through the solution of thermoplastic photo-curable pre-
10 ceramic polymer, applying the pre-preg to a shaped mandrel,
11 using light energy to induce cross-linking of the photo-
12 curable pre-ceramic polymer after application to the
13 mandrel. The thermoplastic pre-ceramic polymer is cured and
14 pyrolyzing the cured thermoplastic pre-ceramic polymer
15 matrix composite material.

16 In a third separate aspect of the invention a
17 single-step process for fabricating continuous ceramic fiber
18 ceramic matrix composites employs a thermoplastic photo-

1 curable pre-ceramic polymer in which the component is shaped
2 by a variety of standard composite fabrication techniques,
3 such as filament winding, tape winding, and woven cloth
4 winding. The process includes steps of passing ceramic
5 fiber monofilament, tow, mat, or woven cloth through a
6 solution of the thermoplastic photo-curable pre-ceramic
7 polymer, applying ceramic fiber monofilament, tow, mat, or
8 woven cloth to a shaped mandrel, using photo-energy of the
9 ultraviolet, visible or infrared light spectrum to induce
10 cross-linking (curing) of the photo-curable pre-ceramic
11 polymer after application to the mandrel and either
12 partially or completely pyrolyzing the now cured pre-ceramic
13 polymer matrix composite material.

14 Other aspects and many of the attendant advantages will
15 be more readily appreciated as the same becomes better
16 understood by reference to the following detailed
17 description.

18 The features of the present invention which are

1 believed to be novel are set forth with particularity in the
2 appended claims.

3 DESCRIPTION OF DRAWINGS

4 Fig. 1 is schematic drawing of an apparatus for making
5 flat plates of ceramic composites from photo-curable pre-
6 ceramic polymers.

7 Fig. 2 is a photograph of the apparatus for making flat
8 plates of Fig. 1.

9 Fig. 3 is schematic drawing of an apparatus for making
10 cylinders of ceramic composites from photo-curable pre-
11 ceramic polymers.

12 Fig. 4 is a photograph of the apparatus for making
13 cylinders of Fig. 3.

14 Fig. 5 is a photograph of a photo-cured pre-ceramic
15 polymer matrix coupon according to the present invention.

16 Fig. 6 is a SEM Photomicrograph at 35X of a fired SiC
17 matrix test coupon prepared from a photo-cured pre-ceramic
18 PECS polymer.

1 Fig. 7 is a SEM Photomicrograph at 350X of a fired SiC
2 matrix test coupon prepared from photo-cured pre-ceramic
3 PECS polymer.

4 Fig. 8 is a SEM Photomicrograph at 1500X of a fired SiC
5 matrix test coupon prepared from photo-cured pre-ceramic
6 PECS polymer.

7 DESCRIPTION OF THE PREFERRED EMBODIMENT

8 A continuous single step manufacturing process for
9 fabricates dense low-porosity composites using novel cross-
10 linkable pre-ceramic polymers and simple plastic industry
11 technology adapted to the thermoset capability of the pre-
12 ceramic polymer. The process eliminates the multi-cycle
13 polymer impregnation pyrolysis method. The process is a
14 simple controllable production process for fiber reinforced
15 ceramic matrix composites, which can be easily automated
16 into large manufacturing continuous processes. This process
17 combines high-yield cross-linkable pre-ceramic polymers and
18 a single step automated process mechanism to produce ceramic

1 components on the scale of aircraft fuselages, boat hulls,
2 and large single ceramic sheets for space vehicle skin
3 panels. The process provides chemically modified pre-
4 ceramic polymers which are very fluid at temperatures 60° C-
5 100° C, have high ceramic yields by weight of 75-95%,
6 exhibit high purity and can be crosslinked into a thermoset
7 with ultraviolet radiation. The process achieves by a
8 series of chemical substitutions using commercially
9 available polymers to incorporate ethynyl side groups on the
10 polymers, which then contain unstable carbon triple bonds
11 and cross-link, by hydrosilylation with Si-H groups upon
12 photo-exposure. The process is to use the chemical
13 substitution ethynyl side group chemistry to produce SiC,
14 Si₃N₄, Al₂O₃ and Al₃N₄ and TiC upon pyrolysis after photo-
15 exposure. Conversion of precursor polymers like
16 polycarbosilane and polysilazane to poly(ethynyl)-
17 carbosilane and poly(ethynyl)silazane achieve this
18 objective. The process draws a fiber, tape, fabric, woven

1 cloth onto a mandrel or suitable substrate by first passing
2 it through the chemically modified pre-ceramic polymer. The
3 objective of this process is to saturate the fiber, tape,
4 fabric, woven cloth with the very fluid pre-ceramic polymer
5 and then photo-cure it on the mandrel or substrate as the
6 saturated material is drawn along by motorized winding or
7 pulling mechanisms known to the prior art. The process
8 provides a continuous fabrication process to enable making a
9 dense (total porosity <8%) fiber reinforced ceramic
10 composite in a single step. This objective is achieved by
11 compacting each layer of pre-ceramic polymer saturated
12 material onto the already pyrolyzed layer below permitting
13 excess polymer to impregnate this layer. The back-fill
14 allowed here reduces the final component porosity, increases
15 strength and provides a short path for volatiles to escape
16 mitigating interlayer delamination. This layer by layer
17 buildup is continued until the required component thickness
18 is reached.

1 The novel nature of the photocurable pre-ceramic
 2 polymer enables a process, which is unique to porous filters
 3 not achievable with conventional pre-ceramic polymers. This
 4 process employs the ability to thermoset the pre-ceramic
 5 polymer into a rubbery hard solid prior to heating. In this
 6 form the pre-ceramic polymer can be heated and subsequently
 7 pyrolyzed without flowing into unwanted areas of the filter.
 8 Because of the ability of this process to produce high yield
 9 beta-SiC in near Si-C stoichiometry a matrix or coating is
 10 formed upon sintering that is highly receptive to heating
 11 with microwave energy. The microwave susceptible porous
 12 filter is ideally suited for trapping particulate from
 13 diesel engine exhausts and can be regeneratively used by
 14 microwave heating to a temperature above the oxidation
 15 threshold of the trapped particulate soot. The pre ceramic
 16 polymer can be made to form not only SiC but also other
 17 ceramic bodies such as Si_3N_4 , BC, LAS, etc.

18 Referring to Fig. 1 in conjunction with Fig. 2 an

1 apparatus 10 for making flat plates of ceramic composites
 2 from photo-curable pre-ceramic polymers includes a frame 11
 3 with a process bed, a set of fabric rollers 12, a set of
 4 guide rollers 13, a set of drive rollers 14, a drive motor
 5 15, a compression roller 16, a process head 17 having a
 6 light-emitting lamp, a furnace 18, a covering 19 and a
 7 source of inert gas and a control panel 20. The source of
 8 inert gas provides an inert atmosphere.

9 Referring to Fig. 3 in conjunction with Fig. 4 an
 10 apparatus 110 for making cylinders of ceramic composites
 11 from photo-curable pre-ceramic polymers includes a dry
 12 nitrogen environmental chamber 111, a fabric roller 112, an
 13 applicator 113 of a photo-curable pre-ceramic polymer, a
 14 take-up mandrel 114, a pressure loaded compaction roller
 15 115, a light-emitting lamp 116 and a consolidation and
 16 pyrolysis zone 117. The consolidation and pyrolysis zone
 17 117 has a heater 118. The fabric roller dispenses woven
 18 ceramic fabric.

1 Commercially available polycarbosilanes and
2 polycarbosiloxane polymers could be rendered photo-curable,
3 by high intensity photo-radiation, through the addition of
4 ethynyl side groups to the polymer. The polymer,
5 poly(ethynyl) carbosilane, is rendered into an infusible
6 thermoset upon photo-radiation. The process is able to
7 similarly elevate ceramic yields to ~85 % by weight.

8 It has been demonstrated that various combinations of
9 di-functional and tri-functional silane precursors can be
10 utilized to enhance cross-linking and elevate ceramic yield.
11 Combinations of dichlorodimethylsilane (di-functional) and
12 trichlorophenylsilane (tri-functional) can be employed.
13 Through the addition of branching, or cross-linking, ceramic
14 yields as high as 77% have been obtained. Further, it is
15 possible to doped these polymers, with boron for example, to
16 control sintering and crystallization behavior.

17 While this process allows the addition of ethynyl side
18 groups to potentially a wide range of available pre-ceramic

1 polymers, there are other methods of directly synthesizing
2 poly(ethynyl)carbosilane, which are outlined below. In both
3 of the following reaction paths, tri-functional organotri-
4 chlorosilanes are utilized, in part or in entirety, to
5 permit the introduction of photo-polymerizable side-groups,
6 such as ethynyl groups derived from the reaction of sodium
7 acetylide with chlorosilane.

8 In the first reaction route, sodium acetylide is
9 reacted with the organotrichlorosilane, such as a methyl- or
10 phenyltrichlorosilane, as shown in step 1. Typically, this
11 is performed in a solvent, such as hexane or methylene
12 chloride. The by-product of this reaction is sodium
13 chloride, which is insoluble and can be easily removed by
14 filtration and/or sedimentation (step 2). The resulting
15 organo(ethynyl)chlorosilane can be reacted directly with
16 sodium which is a Würtz type condensation reaction or mixed
17 with an organodichlorosilane prior to the initiation of
18 polycondensation. Assuming that all "R"s are the same, and

- 1 "a + b = 1", then the following reaction path can be
- 2 proposed:

| Processing Step | Reaction |
|---|---|
| 1. The addition of ethynyl (acetylide) side groups to tri-functional polysilazane reactant. | $a \{ \text{RSiCl}_3 + g \text{ NaC}\equiv\text{CH} \rightarrow$ $\text{RSiCl}_{(3-g)}\text{C}\equiv\text{CH}_g + g \text{ NaCl} \}$ |
| 2. Remove NaCl by filtration. | $- ag \text{ NaCl}$ |
| 3. The addition of di-functional chain former (optional). | $+ b \{ \text{R}_2\text{SiCl}_2 \}$ |
| 4. Condensation of modified precursor solution to produce poly(ethynyl) silazane | $a (\text{RSiCl}_{(3-g)}\text{C}\equiv\text{CH}_g) + b (\text{R}_2\text{SiCl}_2) + 2[a(3-g) +$ $b] \text{Na} \rightarrow 1/n \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{C}\equiv\text{CH}_{ag} \}_n + 2[a(3-$ $g) + b] \text{NaCl}$ |

| | |
|---|--|
| pre-ceramic polymer through the addition of sodium. | |
|---|--|

Table 1: New processing route 1: Steps and reaction chemistries to form poly(ethynyl)carbosilane-- Final Product

$$= 1/n\{\text{SiR}'_{a+2b}\text{C}\equiv\text{CH}_{ag}\}_n.$$

1 In route 1, the photo-cross-linkable ethynyl group
2 (acetylide) is added prior to the initiation of Würtz type
3 condensation reaction. In route 2, a method of adding
4 ethynyl side-groups post-condensation, thereby avoiding the
5 exposure of the ethynyl ligand to sodium during the pre-
6 ceramic polymer synthesis is disclosed. In this process,
7 tri-functional and/or a mixture of di-functional and tri-
8 functional chlorosilanes are reacted with a sub-
9 stoichiometric quantity of metallic sodium, sufficient to
10 bring about an increase in molecular weight and viscosity of
11 the now pre-ceramic polymer backbone, but leaving a fraction
12 of the chlorosilane reaction sites unreacted. The resulting

1 sodium chloride by-product can be removed by filtration
 2 and/or sedimentation (step 2).

3 Following polymer condensation, with unreacted
 4 chlorosilane sites intact, excess sodium acetylide is added
 5 to react with the aforementioned unreacted sites to produce
 6 poly(ethynyl)carbosilane photo-curable pre-ceramic polymer.
 7 The poly(ethynyl)carbosilane pre-ceramic polymer can be
 8 retrieved by solvent evaporation by the application of heat
 9 and/or in vacuo. Assuming that all "R"s are the same, and
 10 "a + b = 1", the final desired reaction product is expressed
 11 in the reaction path below in Table 2.

12 Table 2: New processing route 2: Steps, and reaction
 13 chemistries, to form poly(ethynyl)carbosilane.

| Processing Step | Reaction |
|--|---|
| 1. Mixture of di-functional and tri-functional | $a(RSiCl_3) + b(R_2SiCl_2) + [y/(3a+2b)]Na \rightarrow$ $(1/n) \{ Si_{(a+b)} R_{(a+2b)} Cl_{[(1-y)/(3a+2b)]} \}_n +$ $[y/(3a+2b)] NaCl$ |

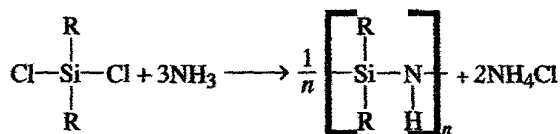
| | |
|---|--|
| chlorosilanes reacted with a sub-stoichiometric amount of sodium (where $y < [3a+2b]$). | |
| 2. Remove NaCl by filtration and/or sedimentation. | $-[y/(3a+2b)] \text{ NaCl}$ |
| 3. Addition of ethynyl side groups to partially condensed polysilazane polymer through the addition of excess sodium acetylide. | $\begin{aligned} & (1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{Cl}_{[(1-y)/(3a+2b)]} \}_n \\ & + [(1-y)/(3a+2b)] \text{NaC}\equiv\text{CH} \rightarrow \\ & (1/n) \{ \text{Si}_{(a+b)} \text{R}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n + \\ & [(1-y)/(3a+2b)] \text{NaCl} \end{aligned}$ |

Product = $(1/n) \{ \text{SiR}_{(a+2b)} \text{C}\equiv\text{CH}_{[(1-y)/(3a+2b)]} \}_n$.

- 1 In the previous section, the method of preparing
- 2 poly(ethynyl)carbosilane, a photo-curable pre-ceramic

1 containing ethynyl group should lead to the addition of
2 approximately 5 to 20 weight percent SiC upon pyrolysis.

3 One of the simplest and direct methods of preparing
4 polysilazane precursors to silicon nitride, with a 70 weight
5 percent ceramic yield is to dissolve dichlorosilane in
6 dichloromethane to yield polysilazane oils. Pyrolysis in
7 flowing nitrogen gas yielded nearly phase pure α - Si_3N_4 after
8 heat treatment at 1150°C for 12 hours. Numerous other
9 permutations and refinements to the preparation of
10 polysilazane oils and polymers have been developed. The
11 reaction path of polysilazane formation using
12 dichlorosilanes and ammonia is set out below:



13 A number of the most direct permutations include
14 the use of trichlorosilanes, methyltrichlorosilanes,
15 dimethyldichlorosilanes, and vinyl-, butyl-, phenyl-, ethyl-

1 , and hexyl- modified chlorosilanes. Increased molecular
 2 weight, and correspondingly increased ceramic yield, can be
 3 achieved by catalytically enhancing the cross-linking during
 4 final polymer preparation. A number of novel methods,
 5 including the use of ruthenium compounds and potassium
 6 hydride have been demonstrated to give ceramic yields upon
 7 pyrolysis as high as 85 percent. The inducement of cross-
 8 linking prior to pyrolysis is essential to achieving the
 9 high ceramic yields necessary to large-scale
 10 commercialization of Si_3N_4 matrix composites for high
 11 temperature applications. The cross-linking methods cited
 12 in the literature, however, are chemical catalysts, making
 13 the shaping and forming processes extremely difficult.

14 A ceramic matrix of predominantly silicon nitride with
 15 about 10-15 % SiC by weight is nearly ideal for fabricating
 16 CMCs. In addition, the catalytic cross-linking of the
 17 polysilazane precursor dramatically increases ceramic yield.
 18 The synthesis route should produce high yield $\text{Si}_3\text{N}_4/\text{SiC}$

1 nanocomposites employing a photocurable pre-ceramic polymer
2 precursor.

3 One possible method would be to synthesize the
4 unmodified polysilazane through the ammonolysis of various
5 chlorosilane reactants in dichloromethane solvent followed
6 by modifying the resulting polysilazanes, using a previously
7 described process of chlorination followed by attachment of
8 the ethynyl through reaction with sodium acetylide. Another
9 alternative approach starts with a variety of dichloro-
10 silanes and/or trichlorosilanes and reacts them with sodium
11 acetylide at various concentrations, followed by ammonolysis
12 to result in the final poly(ethynyl) silazane precursor as
13 specifically detailed in the Table 3 below:

| Processing Step | Reaction |
|---|--|
| 1. addition of acetylide side groups trifunctional polysilazane reactant. | $a \{ \text{RSiCl}_3 + g \text{ NaCCH} \rightarrow$ $\text{RSiCl}_{(3-g)}\text{CCH}_g + g \text{ NaCl} \}$ |

| | |
|--|---|
| 2. remove NaCl by filtration | - g NaCl |
| 2. addition of difunctional chain former | b {R ₂ SiCl ₂ } |
| 3. ammonolysis of modified precursor solution to produce poly(ethynyl)silazane pre-ceramic polymer | $a [\text{RSiCl}_{(3-g)}\text{CCH}_g] + b [\text{R}_2\text{SiCl}_2] + \text{NH}_3$ $\rightarrow b \{[\text{SiR}_2(\text{NH})]_n\} + a \{[\text{RSi}(\text{NH})_{(3-g)}\text{CCH}_g]_m\} + 2[a(3-g) + 2b]\text{NH}_4\text{Cl}$ |

Table 3: Processing steps and reaction chemistries to form poly(ethynyl)silazane

- 1 The following are examples of combining commercially
- 2 available polymers and catalysts to achieve a final photo-
- 3 curable pre-ceramic polymer to SiC ceramics. In order to be
- 4 photo-curable, the polymer requires either double-bonded
- 5 carbons such as Allyl side groups or triple-bonded carbons
- 6 such as acetylide or propargyl side groups. The catalysts
- 7 can include a thermally curable component such as benzoin

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EXAMPLE 1

| Category | Compound | Amount (grams) |
|------------------|---|-------------------|
| Polymer | Allylhydridopolycarbosilane (5% allyl groups) | 2.0 |
| Catalyst | Benzoil Peroxide | 0.02 |
| Photoinitiator 1 | Ciba-Geigy's Irgacure 1800 | 0.02 |
| Photoinitiator 2 | None | None |

EXAMPLE 2

| Category | Compound | Amount (grams) |
|------------------|---|----------------|
| Polymer | Allylhydridopolycarbosilane (5% allyl groups) | 2.0 |
| Catalyst | Benzoil Peroxide | 0.02 |
| Photoinitiator 1 | Ciba-Geigy's Irgacure 1800 | 0.02 |
| RT initiator | N,N-dihydroxyparatoluidine | 0.02 |

EXAMPLE 3

| Category | Compound | Amount (grams) |
|----------|----------|-------------------|
|----------|----------|-------------------|

| | | |
|------------------|---|------|
| Polymer | Allylhydridopolycarbosilane (5% allyl groups) | 2.0 |
| Catalyst | Benzoil Peroxide | 0.02 |
| Photoinitiator 1 | Ciba-Geigy's Irgacure 1800 | 0.01 |
| Photoinitiator 2 | none | None |

EXAMPLE 4

| Category | Compound | Amount (grams) |
|------------------|----------------------------|----------------|
| Polymer | Poly(ethynyl) carbosilane | 2.0 |
| Catalyst | Benzoil Peroxide | 0.02 |
| Photoinitiator 1 | Ciba-Geigy's Irgacure 1800 | 0.02 |
| Photoinitiator 2 | none | None |

EXAMPLE 5

| Category | Compound | Amount (grams) |
|------------------|---|----------------|
| Polymer | Allylhydridopolycarbosilane (5% allyl groups) | 2.0 |
| Catalyst | Benzoil Peroxide | 0.02 |
| Photoinitiator 1 | Camphorquinone | 0.02 |
| Photoinitiator 2 | 2-(dimethylamino)ethyl methacrylate. | 0.02 |

EXAMPLE 6

| Category | Compound | Amount |
|----------|----------|--------|
|----------|----------|--------|

| | | (grams) |
|------------------|---------------------------------------|---------|
| Polymer | Poly(ethynyl) carbosilane | 2.0 |
| Catalyst | Benzoin Peroxide | 0.02 |
| Photoinitiator 1 | Camphorquinone | 0.02 |
| Photoinitiator 2 | 2-(dimethylamino) ethyl methacrylate. | 0.02 |

EXAMPLE 7

| Category | Compound | Amount (grams) |
|------------------|---|----------------|
| Polymer | Allylhydridopolycarbosilane (5% allyl groups) | 2.0 |
| Catalyst | Benzoin Peroxide | None |
| Photoinitiator 1 | Camphorquinone | 0.02 |
| Photoinitiator 2 | 2-(dimethylamino) ethyl methacrylate. | 0.02 |

EXAMPLE 8

| Category | Compound | Amount (grams) |
|------------------|---|----------------|
| Polymer | Allylhydridopolycarbosilane (5% allyl groups) | 2.0 |
| Catalyst | Benzoin Peroxide | 0.02 |
| Photoinitiator 1 | Camphorquinone | 0.01 |
| Photoinitiator 2 | 2-(dimethylamino) ethyl methacrylate). | 0.01 |

EXAMPLE 9

| Category | Compound | Amount (grams) |
|------------------|---|-------------------|
| Polymer | Allylhydridopolycarbosilane (5% allyl groups) | 2.0 |
| Catalyst | Benzoil Peroxide | none |
| Photoinitiator 1 | Camphorquinone | 0.01 |
| Photoinitiator 2 | 2-(dimethylamino)ethyl methacrylate). | 0.01 |

1 All of the above examples cross-linked under photo-
 2 irradiation (using either ultraviolet light or blue light as
 3 indicated) within a few minutes to an hour under continuous
 4 irradiation at room temperature. The samples were
 5 transformed by this method from thermoplastic to thermoset
 6 pre-ceramic polymers which did not flow or deform
 7 significantly upon subsequent heat-treatment and pyrolysis,
 8 ultimately yielding SiC containing ceramics. The examples
 9 are meant to be illustrative. A person trained in the art
 10 can easily modify the ratios and selection of both pre-
 11 ceramic polymer and/or photo-initiators and catalyst
 12 combinations.

1 This process enables the continuous manufacture of
2 fiber reinforced ceramic composites by the use of high
3 ceramic yield pre-ceramic polymers which are photo-curable
4 to a thermoset from a thermoplastic state. A composite in
5 any form or shape is fabricated by photocuring each
6 individual layer of fiber with in-situ pyrolysis of the pre-
7 ceramic polymer impregnated into the fiber layer. The layer
8 by layer of fiber, fabric or woven cloth is pressure loaded
9 to press the thermoplastic polymer infiltrated fabric onto
10 the mandrel or flat substrate thereby permitting excess
11 polymer to impregnate the porous, already pyrolyzed, layer
12 below. This single step process allows a shorter mean free
13 path for volatiles to escape with less destruction than the
14 removal of organics from more massive parts, for
15 consolidation of each layer individually, and for increased
16 layer to layer bonding and improved interlaminar shear
17 strengths.

18 Silicon carbide (SiC) is one of several advanced

1 ceramic materials which are currently receiving considerable
2 attention as electronic materials, as potential replacements
3 for metals in engines, and for a variety of other
4 applications where high strength, combined with low density
5 and resistance to oxidation, corrosion and thermal
6 degradation at temperatures in excess of 1000° C are
7 required. Unfortunately, these extremely hard, non-melting
8 ceramics are difficult to process by conventional forming,
9 machining, or spinning applications rendering their use for
10 many of these potential applications problematic. In
11 particular, the production of thin films by solution
12 casting, continuous fiber by solution or melt spinning, a
13 SiC matrix composite by liquid phase infiltration, or a
14 monolithic object using a precursor-based binder/sintering
15 aid, all require a source of SiC which is suitable for
16 solution or melt processing and which possesses certain
17 requisite physical and chemical properties which are
18 generally characteristic of polymeric materials.

1 Polymeric precursors to ceramics such as SiC afford a
2 potential solution to this problem as they would allow the
3 use of conventional processing operations prior to
4 conversion to ceramic. A ceramic precursor should be
5 soluble in organic solvents, moldable or spinnable,
6 crosslinkable, and give pure ceramic product in high yield
7 on pyrolysis. Unfortunately, it is difficult to achieve all
8 these goals simultaneously. Currently available SiC
9 precursor systems are lacking in one or more of these areas.
10 Problems have been encountered in efforts to employ the
11 existing polysilane and polycarbosilane precursors to SiC
12 for preparation of SiC fiber and monolithic ceramic objects.
13 All of these precursors have C/Si ratios considerably
14 greater than one, and undergo a complex series of ill-
15 defined thermal decomposition reactions which generally lead
16 to incorporation of excess carbon. The existence of even
17 small amounts of carbon at the grain boundaries within SiC
18 ceramics has been found to have a detrimental effect on the

1 strength of the ceramic, contributing to the relatively low
2 room-temperature tensile strengths typically observed for
3 precursor-derived SiC fibers.

4 Efforts to develop polymeric precursors to SiC have
5 focused largely on two types of polymers, polysilanes, which
6 have a Si--Si backbone, and polycarbosilanes, in which the
7 polymer backbone is $[-Si-C-]_n$. The polysilanes all
8 suffer from problems due to insolubility, infusibility
9 and/or excess carbon incorporation. Certain of the
10 polycarbosilanes have more suitable physical properties for
11 processing; however, in general, these also contain a
12 higher-than-1:1 C:Si ratio and incorporate excess carbon on
13 pyrolysis.

14 In the case of the polycarbosilanes, high molecular
15 weight linear polymers of the type $[R_{1.5}SiCH_2]_n$, where R is H and/or hydrocarbon groups, have been
16 prepared by ring-opening-polymerization reactions starting
17 from cyclic disilacyclobutanes using chloroplatinic acid and
18

1 shaped by a variety of standard composite fabrication
 2 techniques, such as filament winding, tape winding, and
 3 woven cloth winding. The process includes steps of
 4 passing ceramic fiber monofilament, tow, mat, or woven cloth
 5 through a solution of the thermoplastic photo-curable pre-
 6 ceramic polymer, applying ceramic fiber monofilament, tow,
 7 mat, or woven cloth to a moving flat substrate and using a
 8 heated or unheated compaction roller to press the
 9 thermoplastic pre-ceramic polymer coated ceramic fiber onto
 10 flat substrate. The process also includes the steps of
 11 using photo-light of the ultraviolet, visible, or infrared
 12 light spectrum to induce cross-linking (curing) of the
 13 photo-curable pre-ceramic polymer thereby rendering a
 14 thermoset polymer and either partially or completely
 15 pyrolyzing the now cured pre-ceramic polymer matrix coated
 16 ceramic fiber material. The pre-ceramic polymer
 17 poly(ethynyl)carbosilane yields silicon carbide upon
 18 pyrolysis. The pre-ceramic polymer may also yield oxide

1 ceramic such as aluminum oxide upon pyrolysis. Other photo-
 2 curable pre-ceramic polymers may yield silicon nitride,
 3 aluminum nitride and titanium carbide, for example.

4 A first process of forming a photo-curable pre-ceramic
 5 polymer, poly(ethynyl)-carbosilane to silicon carbide
 6 ceramic includes the steps of reacting sodium acetylide
 7 with organo-chlorosilanes and condensing (polymerizing) the
 8 resultant organo-(ethynyl)chlorosilane product of step a
 9 with an excess of an alkali metal. The organochlorosilane
 10 is selected from a group of one or more of the following:
 11 dichlorodimethylsilane, trichloro-phenylsilane (tri-
 12 functional), and methyltrichlor.

13 A second process of forming a photo-curable pre-ceramic
 14 polymer, poly(ethynyl)-carbosilane to silicon carbide
 15 ceramic includes the steps of reacting sodium acetylide
 16 with organochloro-silanes and condensing (polymerizing) the
 17 resultant organo(ethynyl)-chlorosilane product of step a
 18 with an excess of an alkali metal sodium.

1 A third process of forming a photo-curable pre-ceramic
2 polymer, poly(ethynyl)-carbosilane, to silicon carbide
3 ceramic includes the steps of reacting sodium acetylide with
4 a mixture of organodichlorosilanes and organo-
5 trichlorosilanes and condensing (polymerizing) the
6 resultant organo(ethynyl)-chlorosilane product of step a
7 with an excess of an alkali metal.

8 A fourth process of forming a photo-curable pre-ceramic
9 polymer, poly(ethynyl)-carbosilane to silicon carbide
10 ceramic includes the steps of reacting a sub-stoichiometric
11 amount of an alkali metal with organochloro-silanes and
12 reacting the partially polymerized polyorganochlorosilane
13 with sodium acetylide. The organochlorosilane is selected
14 from a group consisting of one or more of the following:
15 dichlorodimethylsilane, trichlorophenylsilane (tri-
16 functional) and methyltrichlorosilane.

17 A fifth process of forming a photo-curable pre-ceramic
18 polymer, poly(ethynyl)-carbosilane to silicon carbide

1 ceramic includes the steps of reacting a sub-
2 stoichiometric amount of sodium metal with
3 organochlorosilanes and reacting the partially polymerized
4 polyorganochlorosilane with sodium acetylide.

5 A sixth process of forming a photo-curable pre-ceramic
6 polymer, poly(ethynyl)carbosilane to silicon carbide
7 ceramic includes the steps of reacting a sub-stoichiometric
8 amount of an alkali metal with a mixture of organodichloro-
9 silanes and organotrichlorosilanes and reacting the
10 partially polymerized polyorganochlorosilane with sodium
11 acetylide.

12 A seventh process of forming a photo-curable pre-
13 ceramic polymer, poly(ethynyl)silazane, to silicon nitride
14 ceramic includes the steps of reacting sodium acetylide with
15 organochlorosilanes and condensing (polymerizing) the
16 resultant organo(ethynyl)chlorosilane product of step a with
17 ammonia.

18 An eighth process of forming a photo-curable pre-

1 ceramic polymer, poly(ethynyl)-silazane to silicon nitride
2 ceramic includes the steps of reacting sodium acetylide with
3 organochlorosilanes and condensing (polymerizing) the
4 resultant organo(ethynyl)-chlorosilane product of step a
5 with ammonia.

6 A ninth process of forming a photo-curable pre-ceramic
7 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
8 includes the steps of reacting sodium acetylide with a
9 mixture of organodichlorosilanes and organotrichloro-silanes
10 and condensing (polymerizing) the resultant organo(ethynyl)-
11 chlorosilane product of step a with ammonia. The
12 organochlorosilane is selected from a group consisting of
13 one or more of the following: dichlorodimethylsilane,
14 trichlorophenylsilane (tri-functional) and methyltrichloro-
15 silane.

16 A tenth process of forming a photo-curable pre-ceramic
17 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
18 includes the steps of reacting a sub-stoichiometric amount

1 of ammonia with organochlorosilanes and reacting the
2 partially polymerized polyorganochlorosilazane with sodium
3 acetylide.

4 An eleventh process of forming a photo-curable pre-
5 ceramic polymer, poly(ethynyl)-silazane to silicon nitride
6 ceramic includes the steps of reacting a sub-stoichiometric
7 amount of ammonia with organochlorosilanes and reacting the
8 partially polymerized polyorganochlorosilazane with sodium
9 acetylide.

10 A twelfth process of forming a photo- curable pre-
11 ceramic polymer, poly(ethynyl)-silazane to silicon nitride
12 ceramic includes the steps of reacting a sub-stoichiometric
13 amount of ammonia with with a mixture of organodichloro-
14 silanes and organotrichlorosilanes and reacting the
15 partially polymerized polyorganochlorosilazane with sodium
16 acetylide.

17 A thirteen process for fabricating a ceramic matrix
18 composites includes the steps of preparing a solution of

1 thermoplastic photo-curable pre-ceramic polymer, passing a
 2 pre-preg through the solution of thermoplastic photo-curable
 3 pre-ceramic polymer, applying the pre-preg to a shaped
 4 mandrel, using light energy to induce cross-linking of the
 5 photo-curable pre-ceramic polymer after application to the
 6 mandrel whereby the thermoplastic pre-ceramic polymer is
 7 curved and pyrolyzing the cured thermoplastic pre-ceramic
 8 polymer matrix composite material.

9 A process of forming a photo-curable pre-ceramic
 10 polymer, poly(ethynyl)-carbosilane to silicon carbide
 11 ceramic includes the steps of (a) reacting sodium acetylide
 12 with organo-chlorosilanes and (b) condensing (polymerizing)
 13 the resultant organo-(ethynyl)chlorosilane product of step a
 14 with an excess of an alkali metal. The organochlorosilane
 15 is selected from a group of one or more of the following:
 16 dichlorodimethylsilane, trichloro-phenylsilane (tri-
 17 functional) and methyltrichlorosilane.

18 A process of forming a photo-curable pre-ceramic

1 polymer, poly(ethynyl)-carbosilane to silicon carbide
 2 ceramic includes the steps of (a) reacting sodium acetylide
 3 with organochloro-silanes and (b) condensing (polymerizing)
 4 the resultant organo(ethynyl)-chlorosilane product of step a
 5 with an excess of an alkali metal sodium. The rganochloro-
 6 silane is selected from a group consisiting of one or more
 7 of the following: dichlorodimethylsilane, trichlorophenyl-
 8 silane (tri-functional) and methyltrichlorosilane.

9 A process of forming a photo-curable pre-ceramic
 10 polymer, poly(ethynyl)-carbosilane, to silicon carbide
 11 ceramic includes the steps of (a) reacting sodium acetylide
 12 with a mixture of organodichlorosilanes and organotrichloro-
 13 silanes and (b) condensing (polymerizing) the resultant
 14 organo(ethynyl)-chlorosilane product of step a with an
 15 excess of an alkali metal.

16 A process of forming a photo-curable pre-ceramic
 17 polymer, poly(ethynyl)-carbosilane to silicon carbide
 18 ceramic includes the steps of (a) reacting a sub-

1 stoichiometric amount of an alkali metal with organochloro-
2 silanes and (b) reacting the partially polymerized
3 polyorganochlorosilane with sodium acetylide. The
4 organochlorosilane is selected from a group consisting of
5 one or more of the following: dichlorodimethylsilane,
6 trichlorophenylsilane (tri-functional) and
7 methyltrichlorosilane.

8 A process of forming a photo-curable pre-ceramic
9 polymer, poly(ethynyl)- carbosilane to silicon carbide
10 ceramic includes the steps of (a) reacting a sub-
11 stoichiometric amount of sodium metal with organochloro-
12 silanes and (b) reacting the partially polymerized
13 polyorganochlorosilane with sodium acetylide. The
14 organochlorosilane is selected from a group consisting of
15 one or more of the following: dichlorodimethylsilane,
16 trichlorophenylsilane (tri-functional) and methyltrichloro-
17 silane.

18 A process of forming a photo-curable pre-ceramic

1 polymer, poly(ethynyl)carbosilane to silicon carbide ceramic
2 includes the steps of (a) reacting a sub-stoichiometric
3 amount of an alkali metal with a mixture of organodichloro-
4 silanes and organotrichlorosilanes and (b) reacting the
5 partially polymerized polyorganochlorosilane with sodium
6 acetylide.

7 A process of forming a photo-curable pre-ceramic
8 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
9 includes the steps of (a) reacting sodium acetylide with
10 organochlorosilanes and (b) condensing (polymerizing) the
11 resultant organo(ethynyl)chloro-silane product of step a
12 with ammonia. The organochlorosilane is selected from a
13 group consisting of one or more of the following:
14 dichlorodimethylsilane, trichlorophenylsilane (tri-
15 functional) and methyltrichlorosilane

16 A process of forming a photo-curable pre-ceramic
17 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
18 includes the steps of (a) reacting sodium acetylide with

1 organochlorosilanes and (b) condensing (polymerizing) the
2 resultant organo(ethynyl) chloro-silane product of step a
3 with ammonia. The organochlorosilane is selected from a
4 group consisting of one or more of the following:
5 dichlorodimethylsilane, trichlorophenylsilane (tri-
6 functional) and methyltrichlorosilane

7 A process of forming a photo-curable pre-ceramic
8 polymer, poly(ethynyl)silazane, to silicon nitride ceramic
9 includes the steps of (a) reacting sodium acetylide with a
10 mixture of organodichlorosilanes and organotrichlorosilanes
11 and (b) condensing (polymerizing) the resultant organo-
12 (ethynyl)chloro-silane product of step a with ammonia.

13 A process of forming a photo-curable pre-ceramic
14 polymer, poly(ethynyl)silazane to silicon nitride ceramic
15 includes the steps of (a) reacting a sub-stoichiometric
16 amount of ammonia with organo-chlorosilanes and (b) reacting
17 the partially polymerized polyorganochlorosilazane with
18 sodium acetylide. The organochlorosilane is selected from a

1 group consisting of one or more of the following:
2 dichlorodimethylsilane, trichlorophenylsilane (tri-
3 functional) and methyltrichlorosilane

4 A process of forming a photo-curable pre-ceramic
5 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
6 includes the steps of (a) reacting a sub-stoichiometric
7 amount of ammonia with organochlorosilanes and (b) reacting
8 the partially polymerized polyorganochlorosilazane with
9 sodium acetylide. The organochlorosilane is selected from a
10 group consisting of one or more of the following:
11 dichlorodimethylsilane, trichlorophenylsilane (tri-
12 functional) and methyltrichlorosilane

13 A process of forming a photo- curable pre-ceramic
14 polymer, poly(ethynyl)-silazane to silicon nitride ceramic
15 includes the steps of (a) reacting a sub-stoichiometric
16 amount of ammonia with a mixture of organodichlorosilanes
17 and organotrichlorosilanes and (b) reacting the partially
18 polymerized polyorganochlorosilazane with sodium acetylide.

1 A process for fabricating a ceramic matrix composites
2 includes the steps of (a) preparing a solution of
3 thermoplastic photo-curable pre-ceramic polymer, (b) passing
4 a pre-preg through the solution of thermoplastic photo-
5 curable pre-ceramic polymer, (c) applying the pre-preg to a
6 shaped mandrel, (d) using light energy to induce cross-
7 linking of the photo-curable pre-ceramic polymer after
8 application to the mandrel whereby the thermoplastic pre-
9 ceramic polymer is cured and (e) pyrolyzing the cured
10 thermoplastic pre-ceramic polymer matrix composite material.

11 A first single-step fabrication of continuous ceramic
12 fiber ceramic matrix composites employing a thermoplastic
13 photo-curable pre-ceramic polymer in which the component is
14 shape by a variety of standard composite fabrication
15 techniques, such as filament winding, tape winding, and
16 woven cloth winding includes steps of (a) passing ceramic
17 fiber monofilament, tow, mat, or woven cloth through a
18 solution of the thermoplastic photo-curable pre-ceramic

1 shape by a variety of standard composite fabrication
2 techniques, such as filament winding, tape winding, and
3 woven cloth winding under inert atmosphere includes steps of
4 (a) passing ceramic fiber monofilament, tow, mat, or woven
5 cloth through a solution of the thermoplastic photo-curable
6 pre-ceramic polymer, (b) applying ceramic fiber
7 monofilament, tow, mat, or woven cloth to a shaped rotating
8 mandrel, (c) use of a heated or unheated compaction roller
9 to press the thermoplastic pre-ceramic polymer onto the
10 mandrel, (d) using ultraviolet, visible, or infrared light
11 to induce cross-linking (curing) of the photo-curable pre-
12 ceramic polymer thereby rendering a thermoset polymer, (e)
13 either partially or completely pyrolyzing the now cured pre-
14 ceramic polymer matrix material and (f) followed by the
15 final heat treatment of the shaped ceramic matrix composite
16 "brown body". The pre-ceramic polymer is poly(ethynyl)carbo-
17 silane. The pre-ceramic polymer may yield silicon carbide
18 upon pyrolysis. The pre-ceramic polymer may yield an oxide

1 ceramic upon pyrolysis. The pre-ceramic polymer may yield
2 titanium carbide upon pyrolysis. The pre-ceramic polymer
3 may yield aluminum nitride upon pyrolysis. The pre-ceramic
4 polymer may yield silicon nitride upon pyrolysis. The pre-
5 ceramic polymer may yield aluminum oxide upon pyrolysis.

6 A third single-step fabrication of continuous ceramic
7 fiber ceramic matrix composites employing a thermoplastic
8 photo-curable pre-ceramic polymer in which the component is
9 shape by a variety of standard composite fabrication
10 techniques, such as filament winding, tape winding, and
11 woven cloth winding, includes steps of (a) passing ceramic
12 fiber monofilament, tow, mat, or woven cloth through a
13 solution of the thermoplastic photo-curable pre-ceramic
14 polymer, (b) applying ceramic fiber monofilament, tow, mat,
15 or woven cloth to a moving flat substrate, (c) using a
16 compaction roller to press the thermoplastic pre-ceramic
17 polymer coated ceramic fiber onto flat substrate, (d) using
18 photo-light of the ultraviolet, visible, or infrared light

1 spectrum to induce cross-linking (curing) of the
 2 photo-curable pre-ceramic polymer thereby rendering a
 3 thermoset polymer and (e) either partially or completely
 4 pyrolyzing the now cured pre-ceramic polymer matrix coated
 5 ceramic fiber material. ". The pre-ceramic polymer is
 6 poly(ethynyl)carbosilane. The pre-ceramic polymer may yield
 7 silicon carbide upon pyrolysis. The pre-ceramic polymer may
 8 yield an oxide ceramic upon pyrolysis. The pre-ceramic
 9 polymer may yield titanium carbide upon pyrolysis. The pre-
 10 ceramic polymer may yield aluminum nitride upon pyrolysis.
 11 The pre-ceramic polymer may yield silicon nitride upon
 12 pyrolysis. The pre-ceramic polymer may yield aluminum oxide
 13 upon pyrolysis.

14 Photocurable poly(ethynyl)carbosilane can be
 15 synthesized directly from difunctional and trifunctional
 16 chlorosilane reagents with the addition of sub-
 17 stoichiometric amounts of sodium to form poly(chloro)

1 silanes, followed by the addition of excess sodium acetylide
2 to provide photocurable cross-linking sites.

3 Sodium metal suspension (40 % by weight) in oil was
4 weighed. The suspension was washed three times in xylene and
5 separated by centrifugation. The washed sodium was added to
6 200 ml of xylene in the triple-neck reaction vessel. The
7 refluxed reaction vessel was heated under flowing argon to
8 100°C. The mixture of methylene bromide, dichlorodi-
9 methylsilane, and trichlorophenylsilane was slowly added
10 using a burette. An exothermic reaction ensued and the
11 temperature of reaction vessel contents reached 133oC and
12 the mixture boiled vigorously under reflux for approximately
13 30 minutes. The mixture was stirred for an additional hour
14 while cooling. The dark purple/brown mixture, containing
15 precipitates, was filtered and a clear yellow filtrate was
16 obtained.

17 The resulting poly(chloro)carbosi-lane polymer was
18 extracted from the filtrate by evaporation in a Rotovapor

1 apparatus. The resulting dark yellow viscous polymer was
 2 dissolved in tetrahydrofuran (THF). The appropriate amount
 3 of sodium acetylide powder was dissolved in dimethyl
 4 formamide (DMF) and added slowly to the poly(chloro)carbo-
 5 silane polymer solution and an exothermic reaction occurs
 6 and the color of the polymer solution turned a deep orange.
 7 Reaction byproducts were removed by filtration and the final
 8 poly(ethynyl)carbosilane polymer was obtained.

9 Six different examples of PECS, with varying ethynyl
 10 groups concentrations have been prepared as shown in Table 4
 11 Ethynyl concentration was varied from 0 to 25 percent (by
 12 mole).

13 In order to characterize the molecular weight and
 14 molecular weight distributions of polymers synthesized and
 15 utilized in this study, HPLC was utilized. A carefully
 16 prepared calibration curve was measured using NIST traceable
 17 molecular weight standards and measuring elution time. From
 18 this calibration curve, we were able to estimate the peak

- 1 molecular weight of the PECS synthesized based upon the
- 2 chromatograms.

Table 4: Poly(ethynyl)carbosilane polymers synthesized in this study.

| Poly(ethynyl)carbosilane Synthesis Matrix | | | | | | | | | | | |
|---|--------------------|--------|-----------|--------|--------|-----------|--------|--------|-----------|--------|--------|
| Reactants | | | TRIAL 1 | | | TRIAL 2 | | | TRIAL 3 | | |
| | | | 0%A/100%B | | | 5%A/95%B | | | 10%A/90%B | | |
| | NAME | MW | MOL | ML | GM | MOL | ML | GM | MOL | ML | GM |
| A | TCMS | 149.48 | 0.0000 | 0.0000 | 0.000 | 0.0025 | 0.2936 | 0.374 | 0.0050 | 0.5871 | 0.747 |
| B | DCMS | 129.07 | 0.0500 | 6.0653 | 6.454 | 0.0475 | 5.7621 | 6.131 | 0.0450 | 5.4588 | 5.808 |
| C | Methylene Bromide | 173.85 | 0.0500 | 3.5093 | 8.693 | 0.0500 | 3.5093 | 8.693 | 0.0500 | 3.5093 | 8.693 |
| D | NA | 23 | 0.2000 | | 4.600 | 0.2000 | | 4.600 | 0.2000 | | 4.600 |
| E | NA ACETYLIDE | 48 | 0.0000 | | 0.000 | 0.0025 | | 0.120 | 0.0050 | | 0.240 |
| D | 40% Na-OIL | | | | 11.500 | | | 11.500 | | | 11.500 |
| E | 17.3% NA ACETYLIDE | | | | 0.000 | | | 0.694 | | | 1.387 |
| | | | TRIAL 4 | | | TRIAL 5 | | | TRIAL 6 | | |
| | | | 15%A/85%B | | | 20%A/80%B | | | 25%A/75%B | | |
| | NAME | MW | MOL | ML | GM | MOL | ML | GM | MOL | ML | GM |
| A | TCMS | 149.48 | 0.0075 | 0.8807 | 1.121 | 0.0100 | 1.1742 | 1.495 | 0.0125 | 1.4678 | 1.869 |
| B | DCMS | 129.07 | 0.0425 | 5.1555 | 5.485 | 0.0400 | 4.8523 | 5.163 | 0.0375 | 4.5490 | 4.840 |
| C | Methylene Bromide | 173.85 | 0.0500 | 3.5093 | 8.693 | 0.0500 | 3.5093 | 8.693 | 0.0500 | 3.5093 | 8.693 |
| D | NA | 23 | 0.2000 | | 4.600 | 0.2000 | | 4.600 | 0.2000 | | 4.600 |
| E | NA ACETYLIDE | 48 | 0.0075 | | 0.360 | 0.0100 | | 0.480 | 0.0125 | | 0.600 |
| D | 40% Na-OIL | | | | 11.500 | | | 11.500 | | | 11.500 |
| E | 17.3% NA ACETYLIDE | | | | 2.081 | | | 2.775 | | | 3.468 |

In Table 5 below, several of our polymers are compared with Dow Corning PCS. Our materials were purposely prepared as viscous fluids for greater ease in fabrication.

| POLYMER | ELUTION TIME | MORPHOLOGY | MOLECULAR WEIGHT |
|-----------------|--------------|-------------|------------------|
| Dow Corning PCS | 14.468 | Solid Flake | 4400 |

| | | | |
|----------------------|--------|---------------|------|
| PECS (0% ethynyl) A | 16.598 | Viscous Fluid | 750 |
| PECS (0% ethynyl) B | 16.449 | Viscous Fluid | 700 |
| PECS (5% ethynyl) | 16.050 | Viscous Fluid | 1300 |
| PECS (15% ethynyl) | 16.862 | Viscous Fluid | 600 |
| PECS (20% ethynyl) A | 16.504 | Viscous Fluid | 700 |
| PECS (20% ethynyl) B | 15.973 | Viscous Fluid | 1400 |
| PECS (25 % ethynyl) | 16.732 | Viscous Fluid | 580 |

Table 5: Molecular Weights and HPLC Elution Times (peak) for PECS Synthesized by MATECH and Compared with Dow Corning PCS

1 One of the polymers synthesized as described above was
 2 used to fabricate a ceramic matrix composite using woven
 3 ceramic fabric. 7.0 grams of Poly(ethynyl)carbosilane with
 4 15% ethynyl side-groups for cross-linking was impregnated
 5 into 4 layers of woven ALTEX fabric. The resulting pre-preg
 6 was photocured over night to produce cross-linked matrix and
 7 then fired in Argon gas to 1200oC for one hour. The
 8 resulting product was a ceramic coupon suitable for testing
 9 and evaluation.

1 The polymer synthesized above, 7.0 grams of Poly
2 (ethynyl)carbosilane with 15% ethynyl side-groups for cross-
3 linking was impregnated into 4 layers of woven ALTEX fabric.
4 The resulting pre-preg was photocured over night to produce
5 cross-linked matrix and then fired in Argon gas to 1200oC
6 for one hour. The resulting product was a ceramic coupon
7 suitable for testing and evaluation.

8 The resulting SiC ceramic matrix composite (CMC) has
9 been characterized. After only two processing cycles, the
10 resulting CMC has an apparent density of 2.134 grams/cc and
11 a porosity of 38.24 percent (%). In addition, it exhibits
12 good strength and sounds very much like a ceramic when
13 tapped. Scanning Electron Microscopy (SEM) photomicrographs
14 reveal that the woven fiber tows (of approximately 500 mono-
15 filaments each) are well bonded with minimal porosity, even
16 at high magnification. Large pores are still present
17 between tows, however, which can permit further
18 densification through repeated polymer-impregnation-

1 pyrolysis (PIP) cycles.

2 EXAMPLE 10

3 For 25% ethynyl side-group substitution, 11.50 grams of
4 sodium metal suspension (40 % sodium by weight) in oil was
5 weighed. The suspension was washed three times in xylene and
6 separated by centrifugation. The washed sodium was added to
7 200 ml of xylene in the triple-neck reaction vessel. The
8 refluxed reaction vessel was heated under flowing argon to
9 100° C. A mixture of 8.693 grams methylene bromide, 4.840
10 grams dichlorodimethylsilane, and 1.869 grams trichloro-
11 phenylsilane was slowly added using a burette. An exothermic
12 reaction ensued and the temperature of reaction vessel
13 contents reached 133oC and the mixture boiled vigorously
14 under reflux for approximately 30 minutes. The mixture was
15 stirred for an additional hour while cooling. The dark
16 purple/brown mixture, containing precipitates, was filtered
17 and a clear yellow filtrate was obtained.

18 The resulting poly(chloro)carbosilane polymer was

1 extracted from the filtrate by evaporation in a Rotovapor
2 apparatus. The resulting dark yellow viscous polymer was
3 dissolved in 50 ml tetrahydrofuran (THF). 0.600 grams of
4 sodium acetylide powder was dissolved in 5.0 ml dimethyl
5 formamide (DMF) and added slowly to the poly(chloro)carbo-
6 silane polymer solution and an exothermic reaction occurred
7 and the color of the polymer solution turned a deep purple-
8 red. Reaction byproducts were removed by filtration and the
9 final poly(ethynyl)carbosilane polymer dissolved in THF was
10 obtained. The polymer was then extracted from the filtrate
11 by evaporation in a Rotovapor apparatus, yielding
12 approximately 8.0 grams of poly(ethynyl)carbosilane.

13 EXAMPLE 11

14 For 20% ethynyl side-group substitution, 11.50 grams of
15 sodium metal suspension (40 % sodium by weight) in oil was
16 weighed. The suspension was washed three times in xylene and
17 separated by centrifugation. The washed sodium was added to
18 200 ml of xylene in the triple-neck reaction vessel. The

1 refluxed reaction vessel was heated under flowing argon to
2 100° C. A mixture of 8.693 grams methylene bromide, 5.163
3 grams dichlorodimethylsilane, and 1.495 grams trichloro-
4 phenylsilane was slowly added using a burette. An exothermic
5 reaction ensued and the temperature of reaction vessel
6 contents reached 133°C and the mixture boiled vigorously
7 under reflux for approximately 30 minutes. The mixture was
8 stirred for an additional hour while cooling. The dark
9 purple/brown mixture, containing precipitates, was filtered
10 and a clear yellow filtrate was obtained.

11 The resulting poly(chloro)carbosilane polymer was
12 extracted from the filtrate by evaporation in a Rotovapor
13 apparatus. The resulting dark yellow viscous polymer was
14 dissolved in 50 ml tetrahydrofuran (THF). 0.480 grams of
15 sodium acetylide powder was dissolved in 5.0 ml dimethyl
16 formamide (DMF) and added slowly to the poly(chloro)-
17 carbosilane polymer solution and an exothermic reaction
18 occurred and the color of the polymer solution turned a deep

1 purple-red. Reaction byproducts were removed by filtration
 2 and the final poly(ethynyl)carbosilane polymer dissolved in
 3 THF was obtained. The polymer was then extracted from the
 4 filtrate by evaporation in a Rotovapor apparatus, yielding
 5 approximately 8.0 grams of poly(ethynyl)carbosilane.

6 EXAMPLE 12

7 For 15% ethynyl side-group substitution, 11.50 grams of
 8 sodium metal suspension (40 % sodium by weight) in oil was
 9 weighed. The suspension was washed three times in xylene and
 10 separated by centrifugation. The washed sodium was added to
 11 200 ml of xylene in the triple-neck reaction vessel. The
 12 refluxed reaction vessel was heated under flowing argon to
 13 100°C. A mixture of 8.693 grams methylene bromide, 5.485
 14 grams dichlorodimethylsilane, and 1.121 grams trichloro-
 15 phenylsilane was slowly added using a burette. An exothermic
 16 reaction ensued and the temperature of reaction vessel
 17 contents reached 133oC and the mixture boiled vigorously
 18 under reflux for approximately 30 minutes. The mixture was

1 stirred for an additional hour while cooling. The dark
 2 purple/brown mixture, containing precipitates, was filtered
 3 and a clear yellow filtrate was obtained.

4 The resulting poly(chloro)carbosilane polymer was
 5 extracted from the filtrate by evaporation in a Rotovapor
 6 apparatus. The resulting dark yellow viscous polymer was
 7 dissolved in 50 ml tetrahydrofuran (THF). 0.360 grams of
 8 sodium acetylide powder was dissolved in 5.0 ml dimethyl
 9 formamide (DMF) and added slowly to the poly(chloro)carbo-
 10 silane polymer solution and an exothermic reaction occurred
 11 and the color of the polymer solution turned a deep purple-
 12 red. Reaction byproducts were removed by filtration and the
 13 final poly(ethynyl)carbosilane polymer dissolved in THF was
 14 obtained. The polymer was then extracted from the filtrate
 15 by evaporation in a Rotovapor apparatus, yielding
 16 approximately 8.0 grams of poly(ethynyl)carbosilane.

17 EXAMPLE 13

18 For 10% ethynyl side-group substitution, 11.50 grams of

1 sodium metal suspension (40 % sodium by weight) in oil was
 2 weighed. The suspension was washed three times in xylene and
 3 separated by centrifugation. The washed sodium was added to
 4 200 ml of xylene in the triple-neck reaction vessel. The
 5 refluxed reaction vessel was heated under flowing argon to
 6 100oC. A mixture of 8.693 grams methylene bromide, 5.808
 7 grams dichlorodimethylsilane, and 0.747 grams trichloro-
 8 phenylsilane was slowly added using a burette. An
 9 exothermic reaction ensued and the temperature of reaction
 10 vessel contents reached 133oC and the mixture boiled
 11 vigorously under reflux for approximately 30 minutes. The
 12 mixture was stirred for an additional hour while cooling.
 13 The dark purple/brown mixture, containing precipitates, was
 14 filtered and a clear yellow filtrate was obtained.

15 The resulting poly(chloro)carbosilane polymer was
 16 extracted from the filtrate by evaporation in a Rotovapor
 17 apparatus. The resulting dark yellow viscous polymer was
 18 dissolved in 50 ml tetrahydrofuran (THF). 0.240 grams of

1 sodium acetylide powder was dissolved in 5.0 ml dimethyl
 2 formamide (DMF) and added slowly to the poly(chloro)-
 3 carbosilane polymer solution and an exothermic reaction
 4 occurred and the color of the polymer solution turned a deep
 5 purple-red. Reaction byproducts were removed by filtration
 6 and the final poly(ethynyl)carbosilane polymer dissolved in
 7 THF was obtained. The polymer was then extracted from the
 8 filtrate by evaporation in a Rotovapor apparatus, yielding
 9 approximately 8.0 grams of poly(ethynyl)carbosilane.

10 EXAMPLE 14

11 For 5% ethynyl side-group substitution, 11.50 grams of
 12 sodium metal suspension (40 % sodium by weight) in oil was
 13 weighed. The suspension was washed three times in xylene and
 14 separated by centrifugation. The washed sodium was added to
 15 200 ml of xylene in the triple-neck reaction vessel. The
 16 refluxed reaction vessel was heated under flowing argon to
 17 100°C. A mixture of 8.693 grams methylene bromide, 6.131
 18 grams dichlorodimethylsilane, and 0.374 grams trichloro-

1 phenylsilane was slowly added using a burette. An exothermic
 2 reaction ensued and the temperature of reaction vessel
 3 contents reached 133°C and the mixture boiled vigorously
 4 under reflux for approximately 30 minutes. The mixture was
 5 stirred for an additional hour while cooling. The dark
 6 purple/brown mixture, containing precipitates, was filtered
 7 and a clear yellow filtrate was obtained.

8 The resulting poly(chloro)carbosilane polymer was
 9 extracted from the filtrate by evaporation in a Rotovapor
 10 apparatus. The resulting dark yellow viscous polymer was
 11 dissolved in 50 ml tetrahydrofuran (THF). 0.120 grams of
 12 sodium acetylide powder was dissolved in 5.0 ml dimethyl
 13 formamide (DMF) and added slowly to the poly(chloro)-
 14 carbosilane polymer solution and an exothermic reaction
 15 occurred and the color of the polymer solution turned a deep
 16 purple-red. Reaction byproducts were removed by filtration
 17 and the final poly(ethynyl)carbosilane polymer dissolved in
 18 THF was obtained. The polymer was then extracted from the

1 filtrate by evaporation in a Rotovapor apparatus, yielding
2 approximately 8.0 grams of poly(ethynyl)carbosilane.

3 EXAMPLE 15

4 For 0% ethynyl side-group substitution, 11.50 grams of
5 sodium metal suspension (40 % sodium by weight) in oil was
6 weighed. The suspension was washed three times in xylene and
7 separated by centrifugation. The washed sodium was added to
8 200 ml of xylene in the triple-neck reaction vessel. The
9 refluxed reaction vessel was heated under flowing argon to
10 100°C. A mixture of 8.693 grams methylene bromide, 6.454
11 grams dichlorodimethylsilane was slowly added using a
12 burette. An exothermic reaction ensued and the temperature
13 of reaction vessel contents reached 133oC and the mixture
14 boiled vigorously under reflux for approximately 30 minutes.
15 The mixture was stirred for an additional hour while
16 cooling. The dark purple/brown mixture, containing
17 precipitates, was filtered and a clear yellow filtrate was
18 obtained.

1 The resulting polycarbosilane polymer was extracted
2 from the filtrate by evaporation in a Rotovapor apparatus
3 yielding approximately 8.0 grams of polycarbosilane with no
4 ethynyl side-groups.

5 It has been demonstrated that several commercially
6 available preceramic polymers can be made photocurable. The
7 preceramic polymer CERASETTM SZ inorganic polymer sold by
8 Honeywell Advanced Composites, Inc., which is a silazane-
9 based polymer, can be made photocurable to both UV and blue
10 light through the addition of photoinitiators. Also, the
11 preceramic polymer allylhydridopolycarbosilane (AHPCS)
12 polymer manufactured by Starfire Systems, Inc. can be made
13 photocurable to both UV and blue light through the addition
14 of photoinitiators.

15 EXAMPLE 16

16 A UV light photocurable polysilazane was produced by
17 mixing 2.00 grams of CERASETTM SZ inorganic polymer with
18 0.50 grams of IRGACURE® 1800, manufactured by Ciba Specialty

1 Chemicals, dissolved in 0.50 ml tetrahydrofuran. The
2 resulting yellow fluid, upon exposure to a high intensity UV
3 lamp, became a stiff, rigid polymer within an hour. The
4 resulting cross-linked polymer maintained its shape upon
5 heating and pyrolysis to 1200oC in flowing argon gas. The
6 ceramic yield of the pyrolyzed polymer was in excess of 80
7 percent. A control sample, without the photoinitiator,
8 remained fluid after in excess of 24 hours of continuous UV
9 irradiation.

10 EXAMPLE 17

11 A blue light photocurable polysilazane was produced by
12 mixing 2.00 grams of CERASETTM SZ inorganic polymer with
13 0.50 grams of Camphorquinone, obtained from Aldrich Chemical
14 Company, dissolved in 0.50 ml tetrahydrofuran. The resulting
15 yellow fluid, upon exposure to a high intensity blue lamp,
16 became a stiff, rigid polymer within an hour. The resulting
17 cross-linked polymer maintained its shape upon heating and
18 pyrolysis to 1200oC in flowing argon gas. The ceramic yield

1 of the pyrolyzed polymer was in excess of 80 percent. A
2 control sample, without the photoinitiator, remained fluid
3 after in excess of 24 hours of continuous blue light
4 irradiation.

5 EXAMPLE 18

6 A UV light photocurable allylhydridocarbosilane was
7 produced by mixing 2.00 grams of allylhydridocarbosilane
8 (15% allylchloride) polymer with 0.50 grams of IRGACURE®
9 1800, manufactured by Ciba Specialty Chemicals, dissolved in
10 0.50 ml tetrahydrofuran. The resulting yellow fluid, upon
11 exposure to a high intensity UV lamp, became a stiff, rigid
12 polymer within an hour. The resulting cross-linked polymer
13 maintained its shape upon heating and pyrolysis to 1200°C in
14 flowing argon gas. The ceramic yield of the pyrolyzed
15 polymer was in excess of 80 percent. A control sample,
16 without the photoinitiator, remained fluid after in excess
17 of 24 hours of continuous UV irradiation.

18 EXAMPLE 19

1 A blue light photocurable allylhydridocarbosilane was
2 produced by mixing 2.00 grams of allylhydridocarbosilane
3 (15% allylchloride) polymer with 0.50 grams of Camphor-
4 quinone, obtained from Aldrich Chemical Company, dissolved
5 in 0.50 ml tetrahydrofuran. The resulting yellow fluid,
6 upon exposure to a high intensity blue lamp, became a stiff,
7 rigid polymer within an hour. The resulting cross-linked
8 polymer maintained its shape upon heating and pyrolysis to
9 1200oC in flowing argon gas. The ceramic yield of the
10 pyrolyzed polymer was in excess of 80 percent. A control
11 sample, without the photoinitiator, remained fluid after in
12 excess of 24 hours of continuous blue light irradiation.

13 From the foregoing it can be seen that processes of
14 forming a photo-curable pre-ceramic polymer and their
15 applications have been described.

16 Accordingly it is intended that the foregoing
17 disclosure shall be considered only as an illustration of
18 the principle of the present process.